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RESEARCH ARTICLE

Voltammetric Determination of Diazepam on Antimony Film Screen-Printed Electrode in Pharmaceutical Formulations

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Abstract: ***Background****:* Diazepam belongs to the group of 1,4-benzodiapines. It is used for the treatment of anxiety, convulsions and as a muscle relaxant. The presence of 4,5-azomethine group enables its electrochemical detection.

Introduction*:* A screen-printed electrode modified with antimony film was used for the determination of diazepam in pharmaceutical preparations

Methods: Electrode modification was done by *ex-situ* deposition of antimony on commercially available screen-printed electrode. Parameters affecting the electroanalytical response of the sensor, such as deposition potential, deposition time, and antimony concentration, were examined and optimized. The modified electrode showed enhanced electroactivity for diazepam reduction compared to unmodified electrode. Under optimal conditions, linear sweep voltammetry was used for the determination of analyte.

Results: The sensor showed linear dependence in the range from 0.5 to 10 μmol/L, the correlation coefficient was 0.9992. The limit of detection was 0.33 μmol/L, corresponding limit of quantification was 1.08 μmol/L. Modification enabled determination of diazepam in the presence of oxygen.

Conclusion: The modified electrode was used for the determination of diazepam in tablets. Results confirmed the applicability of the electrochemical sensor.

Keywords: Diazepam determination, antimony film electrode, screen-printed electrode, linear sweep voltammetry.

1. INTRODUCTION

Diazepam (DZP; 7-chloro-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiapon-2-one, Fig. 1) belongs to the group of 1,4-benzodiazepines. It is used for treatment of insomnia, anxiety, epilepsy, alcohol withdrawal and muscular spasms [1]. The consumption of DZP with alcohol increases the sedative effects and its absorption rate, and it can also cause death [2]. Because of that, the scientists are still interested in developing new methods for diazepam determination in both pharmaceutical formulations and biological fluids. Methods such as spectrophotometry [3,4], chromatography [5,6] and electrochemistry [7,8] for determination of DZP are well described in literature.

Fig. 1 Diazepam structure.

Electrochemical determination of DZP is based on reduction of 4,5-azomethine group, yielding dyhidro product. The reduction potential of azomethine group is around -0.7 V, and at more negative potentials the reduction of oxygen, hydrogen ions and/or metal ions may interfere [9]. Hydrogen and metal content can be controlled by pH adjustment or removal of metal ions prior the analysis and oxygen can be removed either by purging the solution with inert gas or by modification of the working electrode. Purging of nitrogen or argon for a few minutes or even overnight is usually enough to remove dissolved oxygen from working solutions [9]. To overcome this problem

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quantification of DZP through oxidation peak after the prereduction of azomethin group is described [1].

Mercury-based electrodes such as mercury film electrodes have been used for determination of both organic and inorganic analytes [10]. Their advantage is application in wide cathodic range, but the major drawback is their toxicity. In the latter years the use of less toxic modifiers such as lead, tin, bismuth, antimony and their alloys were investigated.

Metallic film electrodes were characterized by voltammetry [11,12] and microscopy [11,13] showing that the metallic films were basically uniform. Different films were applied on determination of trace metals by anodic [14,15], cathodic [16], adsorptive stripping voltammetry (AdSV) [17,18], potentiometric stripping analysis (PSA) [19,20] and chronopotentiometry [21]. Besides metals, some authors applied metallic films for determination of organic compounds [22,23].

Deposition of metallic film can be performed by *ex-situ* and *in-situ* technique. The *ex-situ* deposition can be performed in three ways, at constant applied potential, by potential cycling and by galvanostatic deposition. Pauliukaitè and Brett investigated deposition of bismuth on carbon working electrode for determination of heavy metals by square-wave anodic stripping voltammetry (SWASV) [24]. Bismuth films were deposited at -1.4V (vs. standard calomel electrode, SCE) for 300 s in a 1 mg/L Bi(III) in 0.1 mol/L acetate buffer (pH 4.45), by potential cycling between -1.4 and -0.3 V vs. SCE in a 100 mg/L Bi(III) in acetate buffer (pH 4.45) for 20 cycles at a 50 mV/s scan rate. And by galvanostatic deposition in the same acetate buffer containing 100 mg/L Bi(III) by applying current of -10 mA/cm^2 for 300 s. They obtained different sensitivities between deposition technique depending of the metal to be analyzed. In-situ deposition of antimony film on a glassy carbon electrode was performed in 0.01 mol/L hydrochloric acid and 1 mg/L of Sb(III) together with analyzed heavy metals (Cd(II), Pb(II), Bi(III) and Hg(II)) by (ASV) [25]. The authors compared new antimony film electrode (SbFE) with bismuth (BiFE) and mercury (HgFE). They concluded that SbFE was suitable for determination in acidic media (pH $\leq$ 2) in the presence of dissolved oxygen. Compared to bismuth film electrode SbFE is better regarding hydrogen evolution (similar to mercury electrodes). Metallic film electrodes proved to be very convenient for flow injection systems due to their stability [26–28].

In this paper, a modified antimony film screen-printed electrochemical sensor (SbFSPE) was used for determination of DZP in pharmaceutical preparation. The modification of substrate by antimony was optimized regarding the deposition potential, time and amount of modifier in the solution, and the area of electrode was calculated. Deposition of the film was performed in *ex-situ* mode in hydrochloric acid (pH 2).

2. EXPERIMENTAL

2.1. Reagents and chemicals

Stock diazepam solution was prepared by dissolving diazepam standard (Lipomed, Switzerland) in methanol (J.T. Baker, HPLC grade). This solution was stable for one month. Working diazepam solutions were prepared by diluting the stock solution in hydrochloric acid (36.5%, Centrohem, Serbia). Dilution of DZP was made immediately prior to the use. All solutions were kept in the dark.

A standard stock solution of antimony (1000 mg/L atomic absorption standard solution (J.T. Baker)) was diluted as required.

Potassium-hexacyanoferrat(III) was from Kemika, Croatia, and potassium-chloride from Betahem, Serbia (both p.a. grade).

2.2. Apparatus

CHI 800C potentiostat was used for all electrochemical measurements. Screen-printed electrodes were from DropSens DRP-110, working and counter electrodes were made of carbon, and reference was the silver one. Electrodes were used without prior preparation.

2.3. Modification of the SPE

Antimony was deposited on the SPE by applying a constant potential -1.0 V *vs*. Ag/AgCl for 60 s in 5 mg/L antimony solution without stirring. The modified SPE was rinsed with deionized water prior the use.

2.4. Preparation of tablets

For DZP determination in tablets, five tablets of the same mass (2 mg, 5 mg and 10 mg, Hemofarm, Serbia) were powdered in a mortar. 200 mg of powder was accurately weighed and 10 cm^3 of methanol was added. The sample was stirred for ten minutes and then filtered through a filter paper (Whatman no. 42) into a 100 cm^3 volumetric flask. The filtrate was made up to the volume with methanol (methanolic DZP solution). All samples were prepared in triplicate.

For voltammetric analysis, appropriate volume of dissolved tablets (methanolic DZP solution) was diluted with hydrochloric acid so that the final concentration was 0.01 mol/L, and then the concentration of DZP was measured by linear sweep voltammetry (LSV) using external calibration.

2.5. Electrochemical measurements

Cyclic voltammetry (CV) and LSV were used for electrochemical study of DZP. LSV measurements were performed in 0.01 mol/L HCl, sweeping the electrode potential between 0 and -1.0 V at scan rate 100 mV/s. All measurements were performed in triplicate, and values presented in this paper are medium values.

3. RESULTS AND DISCUSSION

3.1. Antimony deposition potential

The potential applied for antimony deposition have significant effect on the structure and quality of the formed antimony film. The unprepared SPE was dipped into antimony solution (50 mg/L) and modified by applying constant potential (-0.8, -1.0 and -1.2 V) for 120 s. The modified electrode was then used for LSV analysis of DZP

solution (10 µmol/L). The Fig. 2 shows obtained results, and it shows that the highest response was achieved at -1.0 V. At more negative potentials hydrogen is reduced, and nascent hydrogen gas may affect the structure of the film. Therefore, for all further experiments -1.0 V potential was used for antimony deposition on a SPE.

Fig. 2 Effect of antimony deposition potential on diazepam determination (50 mg/L Sb(III) for 120 s).

3.2. Antimony deposition time and the concentration of antimony solution

The structure of antimony film is also affected by reduction time and the amount of antimony in the solution. Hence, the following step was to study the reduction time and the antimony concentration. Figure 3 presents sensitivities for DZP reduction obtained for different deposition times (60, 90 and 120 seconds) for 10 µmol/L DZP solution. As it can be seen from the figure 3 the best sensitivity was obtained for 60 s. Longer times weren't investigated as it would significantly increase the preparation time of the modified electrode. The final investigated effect was concentration of antimony. The concentration from 5 to 100 mg/L were used. According to Figure 4 the most sensitive response was obtained when 5 mg/L of antimony was used. Since the current decreases with the antimony concentration increase, it can be concluded that the thickness of antimony film has significant effect on electron transfer between electrode surface and analyte and therefore causing the decrease of sensor sensitivity. From previous experiments can be concluded that deposition of 5 mg/L antimony chloride solution for 60 s at -1.0 V gives the best sensitivity for the reduction of DZP.

Fig. 3 Effect on deposition time on diazepam determination (50 mg/L Sb(III) at -1.0 V *vs*. Ag/AgCl).

Fig. 4 Effect of antimony concentration during deposition on diazepam determination (-1.0 V *vs*. Ag/AgCl during 60 s).

Once the antimony was deposited on SPE, the modified electrode was dipped in a fresh electrolyte solution, and the antimony was stripped off the substrate by applying +0.5V for 300 seconds with stirring and analyzed by atomic absorption spectrometer (AAS). The presence of antimony was confirmed.

The Figure 5 presents linear sweep voltammograms obtained for the reduction of 10 µmol/L DZP on modified (solid line) and unmodified SPE (dotted line). Reduction of DZP (reduction peak at -0.8 V) on unmodified electrode was interfered by oxygen reduction (smaller peak at around -0.65 V). When the same solution was used with SbFSPE the voltammogram (solid line) shows no interference from oxygen and also the increase in cathodic current (by 25%).

Fig. 5 Comparison of linear sweep voltammogram for 10 µmol/L diazepam on bare electrode (solid) and modified (dotted) electrode.

One screen-printed electrode could be used for up to three depositions, with cleaning step after each measurement at +0.5V for 300 seconds. Precision of measurement was

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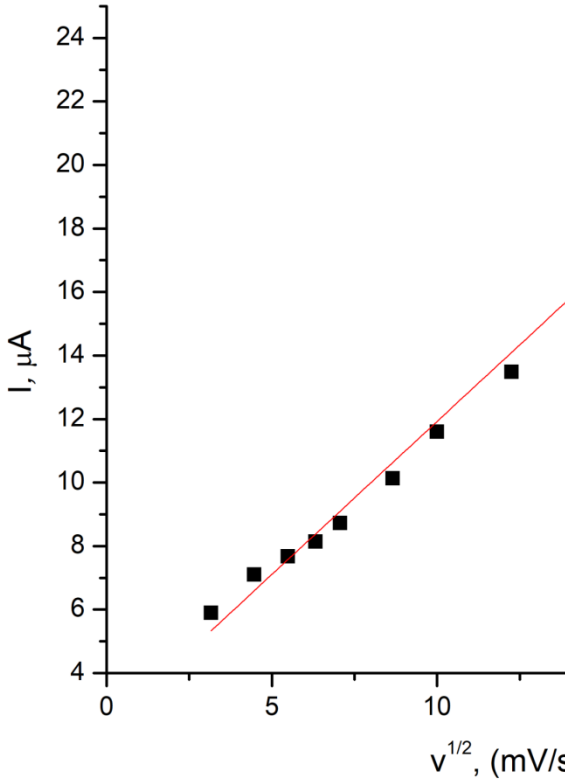

Fig. 7 Obtained linear relationship between cathodic current and square root of applied scan rate.

3.4. Area of the electrode

The electrode surface was obtained by cyclic voltammetry using 1.0 mmol/L $K_3[Fe(CN)_6]$ at different scan rates[29]. For a reversible process, the Randles-Sevcik equation (1) was applied

$$I_{pa} = 2.69 \cdot 10^5 \, n^{3/2} \, A_0 \, D_0^{1/2} \, C_0^{1/2} \qquad (1)$$

Where I_{pa} refers to anodic peak current, n is the number of transferred electrons, A_0 is the surface area of the electrode, D_0 is the diffusion coefficient, C_0 is the concentration of $K_3[Fe(CN)_6]$. For 1 mmol/L $K_3[Fe(CN)_6]$ in 0.1 mol/L KCl as electrolyte, n=1, $D_0=7.6 \cdot 10^{-6}$ cm^2 s^{-1}, from the slope of the plot i_{pa}*versus* $v^{1/2}$ the electroactive area was calculated. The electrode surface for bare SPE was found to be 0.0346 cm^2 and for SbFSPE the surface was calculated 0.0582 cm^2, meaning that the active surface area was increased by 1.7 times.

3.5. Analytical performances

The effect of DZP concentration on cathodic peak current is shown in Figure 8. The response of the detector was linear in the DZP concentration range 0,5 -10 µmol/L and the regression equation I (µA) = (5.19±0.06) c (µmol/L) + (32.3±0.37) and the correlation coefficient was 0.9992 (Fig. 9). The limit of detection (LOD) was calculated to be 0.33 µmol/L and the limit of quantification (LOQ) was 1.08 µmol/L, LOD was calculated as 3σ/slope, where σ is the standard deviation of the y-intercept, and LOQ value was obtained as 10σ/slope. Since there are no reports in literature on the determination of DZP using antimony film electrodes we can compare our results with reports describing application of mercury[30], lead[31] and bismuth[23] modified substrates. Nunes et. al. used hanging mercury drop electrode for voltammetric determination of DZP and clonazepam in natural waters by differential pulse adsorptive

Table 1 Results of DZP determination in tablets (n=3)

Dosage form	Taken conc (µmol/L)	Found conc. (µmol/L)	Recovery (%)	Mean recovery (%)	RSD (%)
Diazepam 2 mg	2.5	2.47	98.80	99.73	1.66
	5	5.10	102.00		0.94
	7.5	7.38	98.40		0.91
Diazepam 5 mg	2.5	2.51	100.40	100.40	2.05
	5	5.08	101.60		1.15
	7.5	7.44	99.20		0.93
Diazepam 10 mg	2.5	2.46	98.40	99.00	1.85
	5	4.87	97.40		1.34
	7.5	7.59	101.20		1.25

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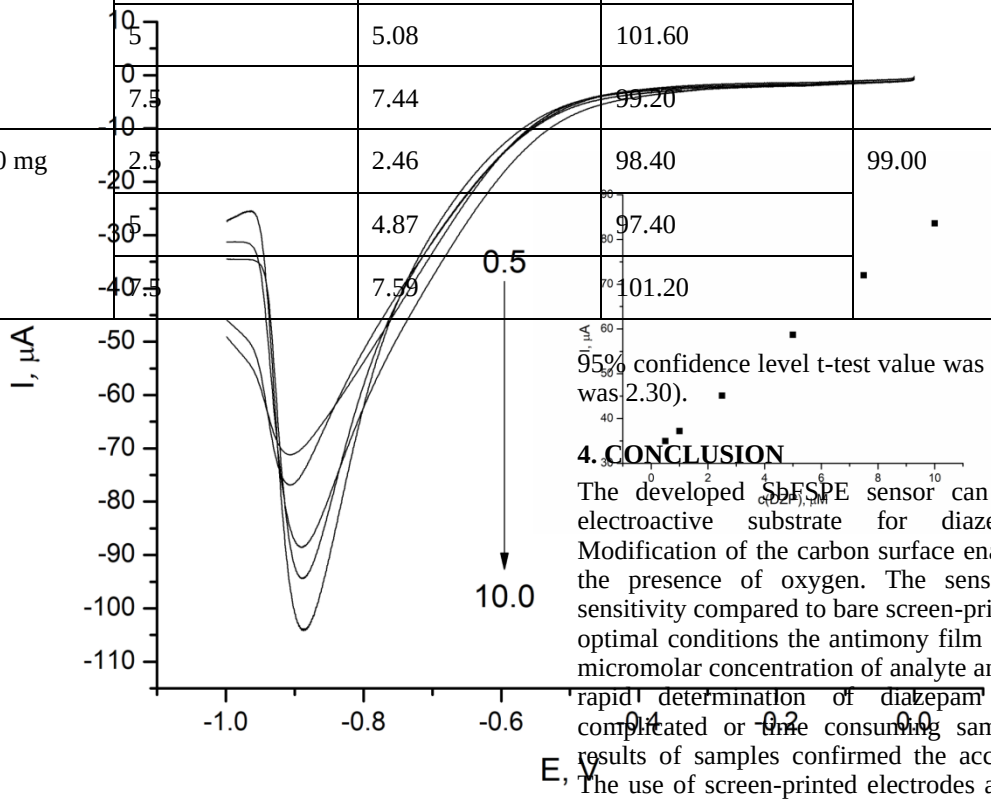

Fig. 8 Linear sweep voltammograms for different diazepam concentrations (0.5 – 10 µmol/L). Insert: calibration graph for diazepam concentrations

3.6. Assay of pharmaceutical preparations

Diazepam tablets, beside the active ingredient, also contain other components. It was important to investigate their effect on electrochemical determination of the analyte. As intereferants the solutions of cellulose, lactose, starch, talk, magnesium-stearate and silicium-dioxide were prepared in hydrochloric acid. In some cases filtration has to be performed. Voltammetric studies of these solutions showed that there is no significant interference for diazepam determination by proposed sensor. The proposed electrochemical detector was used for diazepam determination in commercial tablets. Tablets of different diazepam content were analyzed (2, 5 and 10 mg) and the results were presented in Table 1. There is significant agreement between expected and measured DZP concentration. It was confirmed by student t-test. For the 95% confidence level t-test value was 0.99 (theoretical value was 2.30).

4. CONCLUSION

The developed SbFSPE sensor can be used as a good electroactive substrate for diazepam determination. Modification of the carbon surface enabled determination in the presence of oxygen. The sensor showed increased sensitivity compared to bare screen-printed sensor. Under the optimal conditions the antimony film electrode can measure micromolar concentration of analyte and it can be applied for rapid determination of diazepam in tablets without complicated or time consuming sample preparation. The results of samples confirmed the accuracy of the method. The use of screen-printed electrodes as substrates decreases the price of the sensor and enables its portability.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No animals/humans were used for studies that are the basis of this research.

CONSENT FOR PUBLIVATION

Not applicable.

AVAILABLITY OF DATA AND MATERIALS

The data used and/or analysed during this study are available from the corresponding author on request.

FUNDING

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflicts of interest, financial or otherwise.

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