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Electroanalysis of sulfonamides by flow injection system/high-performance liquid chromatography coupled with amperometric detection using boron-doped diamond electrode☆

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Abstract

Sulfonamides (SAs) were electrochemically investigated using cyclic voltammetry at a boron-doped diamond (BDD) electrode. Comparison experiments were carried out using a glassy carbon electrode. The BDD electrode provided well-resolved oxidation, irreversible cyclic voltammograms and higher current signals when compared to the glassy carbon electrode. Results obtained from using the BDD electrode in a flow injection system coupled with amperometric detection were illustrated. The optimum potential from a hydrodynamic voltammogram was found to be 1100 mV versus Ag/AgCl, which was chosen for the HPLC-amperometric system. Excellent results of linear range and detection limit were obtained. This method was also used for determination of sulfonamides in egg samples. The standard solutions of 5, 10, and 15 ppm were spiked in a real sample, and percentage of recoveries was found to be between 90.0 and 107.7.

Keywords: Sulfonamides; Boron-doped diamond thin film electrode; Cyclic voltammetry; Flow injection system; HPLC; Amperometric detection

1. Introduction

Sulfonamides (SAs) have been used as antibacterial agents for over 60 years. They are often used for prevention or treatment of poultry leucocytozoonosis and coccidiosis, and are generally co-administered in feed. The European Union (EU) has set a maximum residue limit (MRL, 100 ng g^{-1}) for SAs in foods of animal origin such as meat, milk and eggs [1]. Therefore, the determination of such residues in meat and other animal by-products (milk and egg) used for human consumption has become an important task.

Owing to concern over sulfonamide residues in food products of animal origin, a number of techniques have been proposed for their detection, including, immunoassay [2,3], thin layer chromatography (TLC), gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS) [4], capillary electrophoresis [5], and high performance liquid chromatography (HPLC) [6–17] and high performance liquid chromatography–mass spectrometry (HPLC-MS) [18–20]. HPLC with UV and a fluorometry detector were common methods for determining these drugs [6–9]. The alternative for determination of these SAs was HPLC with an electrochemical detector (HPLC-EC) using the amperometric technique [14]. HPLC-EC has been proved to be quite sensitive and inexpensive.

The diamond is one of nature's best insulators, but when doped with boron, the material can possess either semiconducting or semimetallic electronic properties depending on the doping level [21]. Therefore, the boron-doped diamond thin film electrode has shown unique characteristics that make it partic-

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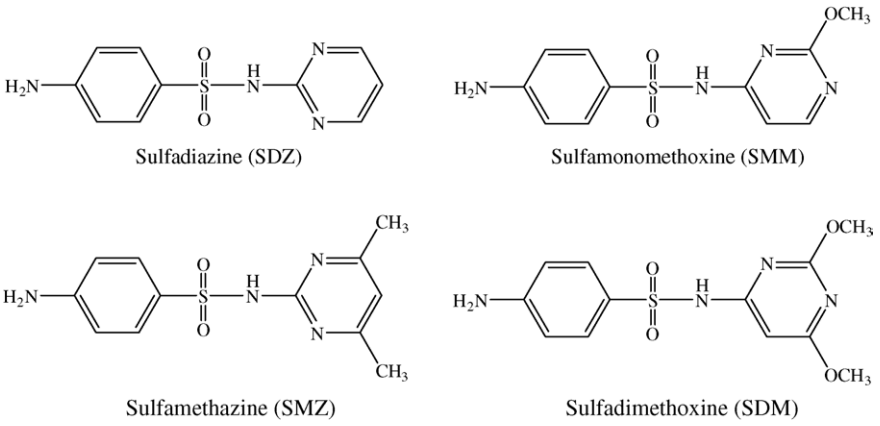

Fig. 1. Chemical structures of four SAs analyzed in this study.

ularly attractive for electrochemical applications, such as: (i) very low and stable voltammetric background current, which results in the improvement of signal-to-background [22,23]; (ii) long-term response stability as well as excellent activity towards any redox species without any pre-treatment [24–27]; (iii) low sensitivity to dissolved oxygen [28]; (iv) a wide working potential window in aqueous solution [29,30]; (v) slight adsorption of polar organic molecules [25]; and (vi) high resistance to deactivation. These material properties are the impetus for our interest in studying and developing diamond electrodes for electrochemical applications. With respect to the outstanding properties of BDD film, quite a number of applications, based on the use of this new material for electrochemical quantitation, have been reported [14,27,31–47]. This synthetic type of diamond film has already been applied as an amperometric detector in flow-injection (FI) analysis [27,31–37,40,42–46] and liquid chromatography [14,37–41,47]. Furthermore, the BDD electrode has been used for the treatment of wastewater [48,49].

This paper reported the use of the BDD electrode to detect four SAs: sulfadiazine, SDZ; sulfamethazine, SMZ; sulfamonomethoxine, SMM; and sulfadimethoxine, SDM. The structures of these four compounds are shown in Fig. 1. Cyclic voltammetry, flow injection analysis and HPLC with an amperometric detector were used in this study. The applicability of the method to analyze hen egg laying samples was demonstrated.

2. Experiment

2.1. Apparatus

The FIA and HPLC system used in this study consisted of a Water Model 510 solvent delivery system (Water Associates Inc, Milford, MA, USA), an injector system (Rheodyne no. 7125) with a 20-μL loop, Inertsil C4 column (GL Science, 150 mm × 4.6 mm i.d.; particle size, 5 μm), a thin layer flow-cell (GL Science Inc.), and an amperometric detector (Autolab Potentiostat 30; Metrohm, Switzerland). The following apparatus used in the sample preparation comprised a mini centrifuge (Cole Parmer, USA); an ultrasonic-homogenizer (Ney Dental, USA); Mixer (National, Matsushita Electric industrial Co. Ltd., Japan); and a micro-centrifugal ultrafilter unit (Ultrafree-MC/PL, regenerated cellulose ultra-filtration membrane, nominal molecular mass limit = 5000, capacity ≤0.5 mL, Millipore, Bedford, MA, USA).

2.2. Reagents

HPLC grade acetonitrile and ortho-phosphoric acid were purchased from Merck (Darmstad, Germany). Deionized water was from a Milli-Q-gradient system (Millipore, $R \geq 18.2\,M\Omega$ cm). Sodium dihydrogen orthophosphate 1-hydrate and disodium hydrogen phosphate were purchased from BDH (VWR international Ltd., England). SMM, SDM, SMZ and SDZ standards were obtained from Sigma (St. Louis, MO, USA). Stock standard solution (500 ppm) of each SA was prepared in acetonitrile:deionized water (50:50, v/v). The stock standards were stored at 4 °C. Working mixed standard solutions of these four SAs were prepared by diluting the stock solutions with 0.1 M phosphate solution.

2.3. Electrode

The BDD electrode grown on conductive Si (1 0 0) substrate using the microwave plasma-assisted chemical vapor deposition (MPCVD) system was obtained from Associate Professor Yasuaki Einaga's laboratory [23]. A mixture of acetone and methanol at a ratio of 9:1 (v/v) was used as the carbon source. B_2O_3, used as the boron source, was dissolved in the acetone–methanol solution at a B/C atomic ratio of 1:100. The BDD electrode was rinsed with isopropanol and then deionized water prior to use.

The glassy carbon (GC) electrode was purchased from Bioanalytical System Inc. (area 0.07 cm^2). It was pre-treated by sequential polishing with 1 and 0.3 μm of alumina/water slurries on felt pads, followed by rinsing with deionized water prior to use.

2.4. Electrochemical measurements

2.4.1. Cyclic voltammetry

Electrochemical measurements were carried out in a single compartment three-electrode glass cell, with a volume of

50 mL. The BDD electrode was pressed against a smooth ground joint at the bottom of the cell, and isolated by an O-ring (area 0.07 cm^2). Ohmic contact was made by placing the backside of the Si substrate onto a brass plate. The GC electrode was also used as a working electrode in a comparison study with the BDD electrode. A platinum wire and Ag/AgCl with a salt bridge were used as the counter and reference electrodes, respectively. Cyclic voltammetry was performed with an Autolab Potentiostat 30. The electrochemical equipment was housed in a faradaic cage to reduce electronic noise.

2.4.2. Flow injection and HPLC analysis with amperometric detection

The measurements (FIA) using the BDD electrode as an amperometric sensor were carried out in a 0.1 M phosphate solution (pH 3.0) at an applied potential of 1100 mV versus Ag/AgCl. The FIA and HPLC system used in this study consisted of a Water Model 510 solvent delivery system, with a flow rate of 1.0 mL min^{-1}; the length of the tubing connecting the injector and the detector in the flow injection system was 20 cm, an injector system, with a 20-μL loop; a thin layer flow-cell; and an amperometric detector. The potential of the electrochemical detector was set using a computer-controlled potentiostat. The thin layer flow-cell consisted of the Ag/AgCl reference electrode and a stainless steel counter electrode. A 1-mm thick silicon rubber gasket was used as a spacer in the cell. The geometric area of the electrode in the cell was estimated at 0.6 cm^2. During the measurements, the flow cell was maintained at room temperature (25 ± 1 °C). An Intertsil C4 column was used for the separation of the SAs. The 0.1 M sodium dihydrogen phosphate (pH 3.0), acetonitrile (80:20; v/v), was used as the mobile phase for FIA experiments, and eluent in the liquid chromatographic experiments.

2.5. The preparation of egg samples

This method used less organic solvent [16]. An accurate 0.2 g of the sample was taken into a 1.5 mL micro-centrifuge tube and homogenized in 0.4 mL of 10% (v/v) perchloric acid solution (in water) with an ultrasonic-homogenizer for 1 min. Next, this micro-centrifuge tube was centrifuged at 6000 rpm for 3 min. A 0.3 mL portion of supernatant liquid was put into an Ultrafree-MC/PL and centrifuged at 6000 rpm for 5 min. The 20 μL of solution in ultra-filtrate was injected into the HPLC system.

2.6. Recovery test

The recoveries of SAs were determined from three egg blank samples, accurately weighed at 1.0 g, and each spiked with mix standards for a concentration of 5, 10, and 15 ppm, respectively. Then an accurate 0.2 g homogenate was transferred into a 1.5 mL micro-centrifuge tube and homogenized in 0.4 mL of 10% (v/v) perchloric acid solution (in water) with an ultrasonic-homogenizer for 1 min. Preparation steps for the egg samples followed.

3. Results and discussion

3.1. pH dependence study

In initial experiments, the electrochemical behavior of four SAs was investigated at the BDD electrode in 0.1 M phosphate solution from pH 2.0 to 7.0. Cyclic voltammograms of SAs at various pH phosphate solutions were obtained. It was found that changing pH phosphate solution effected the oxidation peak current. The best-resolved and highest anodic signals of SAs were obtained at pH 3. Therefore, pH 3 was chosen as the optimal pH.

3.2. Cyclic voltammetry

Fig. 2A and B show the cyclic voltammograms for 50 μM SDM together with the corresponding background voltammogram in 0.1 M phosphate solution (pH 3.0) at the BDD and GC electrodes. The background current for the GC electrode was ∼10 times higher than that obtained from the BDD electrode. The BDD exhibited a well-defined irreversible oxidation peak at ∼1100 mV versus Ag/AgCl, whereas the GC electrode provided an ill-defined irreversible oxidation peak. No cathodic peak was

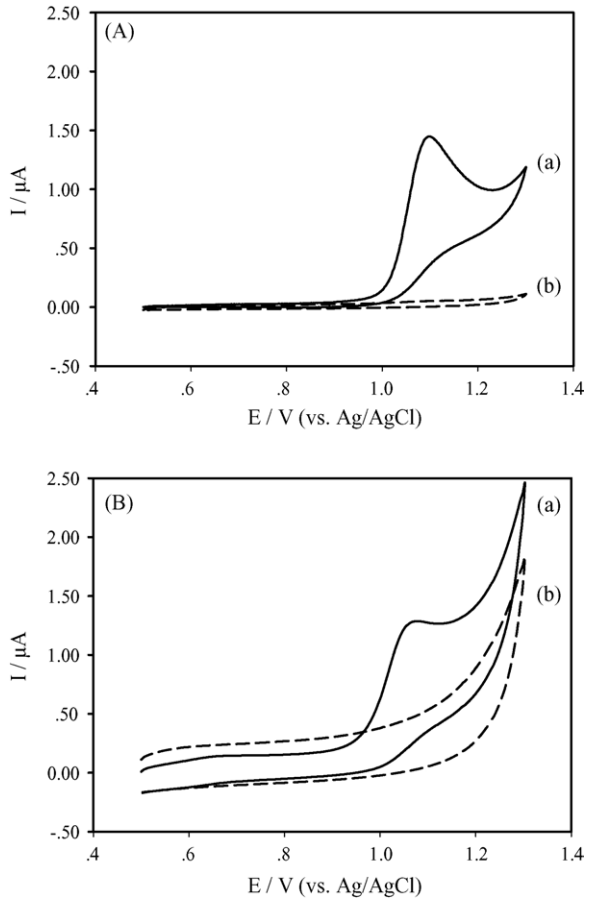

Fig. 2. Cyclic voltammograms for (A) BDD and (B) GC electrodes vs. Ag/AgCl in 50 μM SDM in 0.1 M phosphate solution pH 3.0 (a) and 0.1 M phosphate solution pH 3.0 (b). The sweep rate was 50 mV s^{-1}. The area of electrodes was 0.07 cm^2.

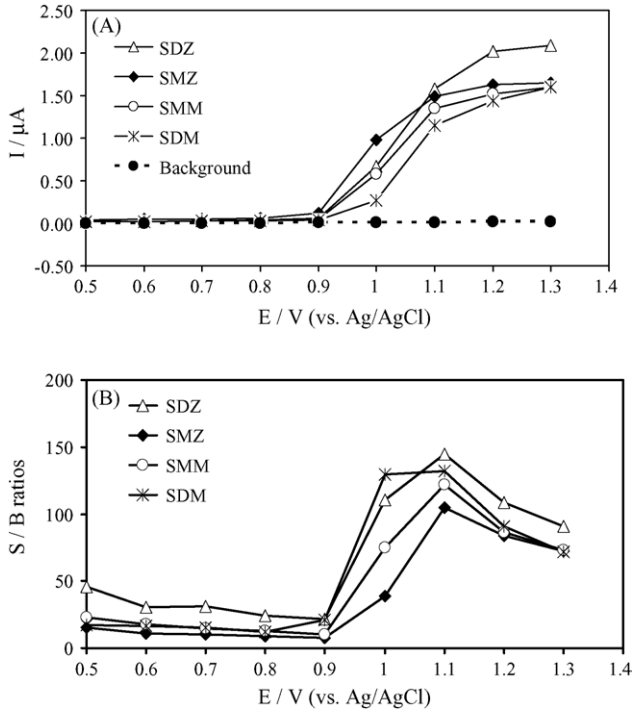

Fig. 3. Hydrodynamic voltammetric results for 10 ppm of each SA. The average peak current obtained from injections ($n = 4$) of (A) background (0.1 M sodium dihydrogen phosphate (pH 3.0):ACN (80:20; v/v), SDZ, SMZ, SMM and SDM in 0.1 M sodium dihydrogen phosphate (pH 3.0):ACN (80:20; v/v). Phosphate solution was used as a carrier stream. The flow rate was 1 mL min^{-1}. (B) Hydrodynamic voltammogram of signal-to-background ratios.

observed at either electrode on the reverse scan within the investigated potential range (+500 to +1300 mV).

3.3. Flow injection analysis with amperometric detection

To obtain the optimal potential for amperometric detection in flow injection analysis, the hydrodynamic behavior of SAs was studied. Fig. 3 shows a hydrodynamic voltammetric *I–E* curve obtained at the BDD electrode for 20 μL injections of 10 ppm to each SA in 0.1 M sodium dihydrogen phosphate (pH 3.0):ACN (80:20; v/v) as the carrier solution. Each datum represents the average of four injections. The absolute magnitude of the background current at each potential is also shown for comparison. The S/B ratios were calculated from Fig. 3A at each potential to obtain the maximum potential point. The hydrodynamic voltammetric S/B ratios versus potential curve are shown in Fig. 3B, with the maximum S/B ratio at 1100 V. Hence, this potential was set for quantitative amperometric potential detection in HPLC analysis experiments.

3.4. HPLC analysis with amperometric detection

In previous papers [7–10] on reversed-phase HPLC analysis of SAs, the C18 or C8, non-polar sorbent columns were used the most frequently. The C18 and C8 sorbents required a large volume of strong elution solvents as the mobile phase. The separation in this experiment was performed using a C4 column, which remarkably reduced the volume of elution solvents required and provided a high signal and clear separation, as described previously [15–17].

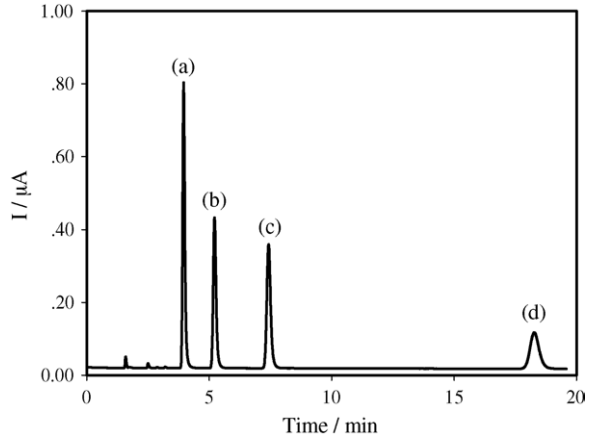

Fig. 4. HPLC-EC chromatogram of a standard mixture containing 10 ppm concentration of (a) SDZ; (b) SMZ; (c) SMM; and (d) SDM at the BDD electrode. The mobile phase was 0.1 M sodium dihydrogen phosphate (pH 3.0):ACN (80:20; v/v). The injection volume was 20 μL, and the flow rate 1 mL min^{-1}.

The results were analyzed by a chromatographic technique (HPLC), coupled with amperometric detection on the BDD electrode. The pH of the mobile phase was selected at 3.0 in order to reduce the above information. The chromatogram of standard solution of the four SAs in 0.1 M sodium dihydrogen phosphate (pH 3.0):ACN (80:20; v/v) solution, as the mobile phase, is presented in Fig. 4. The retention times of the four SAs; SDZ, SMZ, SMM, and SDM, at a concentration of 10 μg mL^{-1}, were 4.0, 5.2, 7.5, and 18.0 min, respectively. Twenty minutes were required to complete separation of the four SAs.

3.5. Method characteristics

The calibration characteristics of the SAs at the BDD electrode are shown in Table 1. The detection limit (DL) and quantitative limit (QL) for the four SAs under these experimental conditions were obtained from $DL = 3S_B/b$ and $QL = 10S_B/b$, when S_B was the standard deviation of the mean value for 10 signals of the blank and b was the slope of the straight line in the analytical curve [50].

From the standard deviation (S_B), the straight line slope of the analytical curve (b), the calculated value of DL and the QL is shown in Table 1. The current responses of SAs var-

Table 1
Linear range (LR), detection limit (DL), slope (b), and quantitative limit (QL) of SDZ, SMZ, SMM, and SDM

SAs	LR (ppm)	Equation $y = bx + a$	R^2	DL (ppm)	QL (ppm)
SDZ	0.050–100	$y = 0.2922x + 0.6232$	0.9905	0.011	0.037
SMZ	0.050–100	$y = 0.2915x + 0.1610$	0.9974	0.012	0.040
SMM	0.050–100	$y = 0.2939x + 0.3084$	0.9959	0.011	0.037
SDM	0.100–300	$y = 0.2898x + 0.6433$	0.9910	0.032	0.107

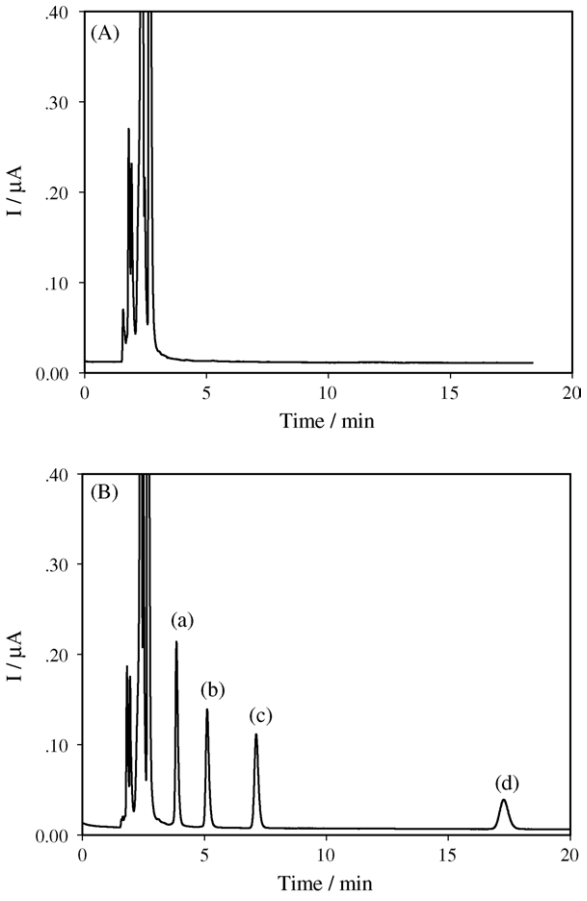

Fig. 5. HPLC-EC chromatograms obtained from egg samples: (A) blank egg sample and (B) egg sample spiked to a 10 ppm concentration of (a) SDZ; (b) SMZ; (c) SMM; and (d) SDM at the BDD electrode. The mobile phase was 0.1 M sodium dihydrogen phosphate (pH 3.0):ACN (80:20; v/v). The injection volume was 20 μL, and the flow rate 1 mL min^{-1}.

ied linearly with the standard concentrations, covering a range of 0.05–100 ppm for SDZ, SMZ and SMM, and 0.1–300 ppm for SDM. The results indicated that this proposed method can be applied for the determination of four SAs in egg samples.

3.6. Application

Egg samples were analysis by the HPLC/EC system. Fig. 5 shows clearly the chromatograms, with clear/sharp peaks and short retention times by using a C4 column and an isocratic mobile phase of 0.1 M sodium dihydrogen phosphate (pH 3.0):ACN (80:20; v/v). The experiment was repeated three times in order to assess the reproducibility in real sample. The recoveries of four SAs were determined by injecting a blank egg sample, spiked together with the standard samples. The recoveries and %R.S.D. of SDZ, SMZ, SMM, and SDM at three different spiked levels are summarized in Table 2. This procedure allowed rapid and efficient purification of SAs and resulted in high recovery (Mean of percentage of recoveries was found to be between 90.0 and 107.7) and reproducibility (%R.S.D. < 4.9% and S.D. < ± 4.7).

Table 2
Analysis four SAs in egg samples ($n = 3$)

SAs	Mean of percentage recovery ($x \pm$ S.D.)			%R.S.D.		
	5 ppm	10 ppm	15 ppm	5 ppm	10 ppm	15 ppm
SDZ	103.0 ± 4.7	96.9 ± 1.9	93.3 ± 1.6	4.5	2.0	1.7
SMZ	107.7 ± 3.8	98.8 ± 2.3	95.3 ± 2.1	3.5	2.3	2.2
SMM	103.2 ± 2.9	94.9 ± 2.3	91.3 ± 1.9	2.8	2.4	2.1
SDM	94.7 ± 1.2	90.0 ± 2.5	95.0 ± 4.7	1.3	2.8	4.9

4. Conclusions

BDD electrodes exhibit excellent performance for the electrochemical detection of SAs (SDZ, SMZ, SMM, and SDM) in egg samples. The optimum potential from the hydrodynamic voltammogram was found to be 1100 mV versus Ag/AgCl, which was chosen for the HPLC-amperometric system. An excellent linearity, and detection and quantitation limit were obtained. This proposed method was used for determination of SAs in egg samples. Percentage recoveries were found to be acceptable.

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