Electrochemical Behavior and the Determination of Furan in Beverage Samples Using Glassy Carbon Electrode

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ABSTRACT: Furan is a possible human carcinogen in many types of foods. A new and sensitive electroanalytical method for determination of furan has been developed and validated. The best condition for electrochemical response was obtained with 0.1 M britton-rabinson buffer solution (pH=5) a glassy carbon electrode (GCE) was used as the working electrode, a Ag/AgCl KCl(sat.) electrode served as the reference electrode, and a platinum wire as the auxiliary electrode under the Differential Pulse Voltammetry (DPV) mode. The peak current obtained from DPV was linearly dependent on the Furan concentration in the range 12–360 µM (0.81–24.5 ppm) with correlation coefficients of 0.999 and a limit of detection (LOD) of 3 µM (0.2 ppm) and limit of quantification (LOQ) of 10 µM (0.68 ppm) were calculated, respectively. The values of the electron-transfer coefficient (a) involved in the rate determining step calculated from the linear plots of Ep against ln (ν) in the pH range investigated were 0.8 confirming the irreversible nature of the oxidation peak. The reproducibility of the method was tested by analyzing 10 samples containing 30 µM of Furan. The RSD % of the method thus obtained was 3.0 % which showed excellent reproducibility for this developed methods.

Key words: Furan, Electrochemical studies, Differential pulse voltammetry, Beverage Samples

INTRODUCTION

As a result of industrialization, synthetic chemicals have imposed adverse effects on human beings and other organisms (Vinodhini and Narayanan, 2009; Agbozu and Opuene, 2009; Abdullahi et al., 2009; Aktar et al., 2009; Chibunda, 2009; Hasan et al., 2010; Sadashiva Murthy et al., 2009; Dutta and Dalal, 2008; Srivastava et al., 2008; Banaee et al., 2008; Asi et al., 2008; Wasim Aktar et al., 2008; Priju and Narayana, 2007; Jafari and Ebrahimi, 2007; Nasrollahzadeh et al., 2007; Shahidi Bonjar, 2007; Shegefti et al., 2010; Adjei-Boateng et al., 2010; Belarbi and Al-Malack, 2010; Hassani et al., 2010; Ghaderi et al., 2012). Furan is a heterocyclic organic compound, consisting of a five-membered aromatic ring with four carbon atoms and one oxygen. The class of compounds containing such rings is also referred to as furans. Furan is a colorless, flammable, highly volatile liquid with a boiling point close to room temperature. It is soluble in common organic solvents, including alcohol, ether and acetone, but is insoluble in water (Jakubke and Jeschkeit 1994). It is toxic and may be carcinogenic. Furan is used as a starting point to other specialty chemicals (Hoydonckx et al., 2005). Furan is used as an intermediate in the synthesis of many chemicals and pharmaceutical agents such as solvents, resins, and lacquers (Carfagna et al., 1993). Furan yields a tumor incidence, where more than 90% of the tumors are adenocarcinomas, and the remainders are squamous cell tumors. In rats, furan induces cholangiocarcinomas, which are tumors that arise from the intrahepatic epithelium. Cholangiocarcinomas tend to grow slowly and to infiltrate the surrounding hepatic parenchyma (NTP, 1993). Furan is formed in many common foods during the thermal treatment of either ascorbate, carbohydrates (with or without amino
acids), unsaturated fatty acids, carotenes, or organic acids (Becalski and Seaman, 2005). During recent decades, a variety of pioneer methods for detection of xenobiotics have been introduced (Ashraf et al., 2012; Clemente et al., 2012; Shwetha et al., 2012; Maheswari and Ramesh, 2012; Garcia-Flores et al., 2013; Etale and Drake, 2013; Ashan and Del Valls, 2011; Annabi et al., 2011; Kapdan et al., 2011; Chen et al., 2011; Akhtar and Tufail, 2011; Naim et al., 2011; Heidari et al., 2011; Saeedi et al., 2013; Jovic et al., 2013; Bhuvaneshwari et al., 2013; Olivalla et al., 2013; Blagovevic et al., 2012; Lopez-Pineiro et al., 2012; Sotelo et al., 2012). There are currently a large number of analytical methods for the determination of furan in foods, the analytical problems first reported (Senyuva, and Gökmen, 2005; Goldmann et al., 2005; Bianchi et al., 2006; Hasnip et al., 2006; Wenzl et al., 2007; Sarafraz-Yazdi et al., 2012; Sid kalal et al., 2012; Byrns et al., 2006; Fan, 2005; Kallio et al., 1989; Locas et al., 2004; Maga, 1979; Mark et al., 2006; Merritt et al., 1963; Persson et al., 1973; Stoffelsma et al., 1968; Tatum et al., 1969; Zöller et al., 2007). In recent years, the electrochemical techniques have led to the advancement in the field of analysis because of their sensitivity, low cost and relatively short analysis time, as compared with other techniques. Electrochemical have proven to be useful for development of very sensitive and selective methods for the determination of organic molecules. In this work, differential pulse voltammetry (DPV) was method with good precision and accuracy for the determination of furan in beverage samples developed.

MATERIALS & METHODS

Furan (>99.0% purity), was purchased from Merck and Co. Inc. (Darmstadt, Germany).

A stock solution of furan (1mM) was prepared in methanol-water (10:90, v/v),britten-rabinson buffers from pH 2.0-10 (0.1 M) which used for pH experiment and also supporting electrolyte, were prepared in doubly distilled water. All other reagents were of analytical grade and obtained from Merck, and all solutions were prepared with doubly distilled water. Voltammetric experiments were performed using a µAutolab Type III electrochemical system. A conventional three-electrode cell consisting of a glassy carbon working electrode (2 mm in diameter), a platinum wire counter electrode and a saturated Ag/AgCl reference electrode were used for voltammetric experiments. A digital pH-meter (Ion Analyzer 827, Metrohm) with precision of ±0.001 was used for pH measurements. All the experiments carried out at room temperature. Before each experiment and transferring the glassy carbon electrode to the solution, it was cleaned by polishing with 0.05µm alumina slurry on a polishing cloth and rinsed thoroughly with doubly distilled water. After each polishing step to get a stable and reproducible background current, Cyclic voltammetry were performed at scan rate of 100 mV/s between 0.0 and 1.6 V for 10 times in 0.1 M H2SO4 solution (Bagheri and Hosseini 2012). To study the accuracy and repeatability of the developed method, carried out using the standard addition method by adding the known amounts of Furan to the pre-analyzed samples then mixtures were analyzed by the developed method.

RESULTS & DISCUSSION

In order to understand the electrochemical process occurring at the GCE (glassy carbon electrode), cyclic voltammetry were applied. Fig.1 shows a cyclic voltammogram of 1mM Furan in 0.1 M britton-rabinson buffer solution (pH=5) at a glassy carbon electrode at 50 mv/sscan rate. As shown in Fig. 1, Furan gives one well-defined irreversible oxidation peak at +1.44 V. The effect of supporting electrolytes on current–potential curves was investigated by a 0.1 M solution of various supporting electrolytes (Fig.2). The results showed that the britton-rabinson buffers can give the best background and signal response. For studying the effect of pH of britton-rabinson buffer solution on voltammetric response of Furan, the cyclic voltammograms of 1.0 mM Furan were recorded from pH 2.0 to 10.0 at a scan rate of 50.0 mV/s. The anodic peak current was affected by the pH of the solution (Figs.3-4). As Fig. 4 shows, the maximum peak current was obtained at pH 5.0. So pH 5.0 was chosen for the subsequent analytical experiments. Useful data involving electrochemical mechanism mostly can be acquired from the scan rate and its relationship with peak current and potential. Therefore, the influence of potential scan rate on the electrochemical behavior of Furan at GCE was studied with the change of scan rate (Fig. 5A). As shown Fig. 5A, when the scan rate was increased, a linear relationship between the peak current and thesquare root of scan rate (Fig. 5B) in the range from 25 to 250 mV/s was obtained, suggesting a diffusion-controlled process for oxidation of furan at GCE.

A plot of logarithm of anodic peak current vs. logarithm of scan rate gave a straight line with a slope of 0.612 (Fig. 6A) closes to the theoretical value of 0.5, which is expected for an ideal reaction for the diffusion-controlled electrode process (Laviron et al., 1980; Hegde, et al., 2009). In addition, the Ep of the oxidation peak was dependent on scan rate. The anodic peak potential shifted to positive values when the scan rate was increased, which these results also confirmed that the oxidation reaction was irreversible (Fig. 6B).
Fig. 1. A cyclic voltammogram of 1 mM Furan solutions in methanol-water (10:90) and 0.1 M Britton-Rabinson buffer solution (pH=5) at a GCE and 50 mV/s scan rate to the Ag/AgCl reference electrode.

Fig. 2. Cyclic voltammograms of Furan with 0.1 M solution of various supporting electrolytes.

Fig. 3. DPVs of 1 mM Furan solutions in methanol-water (10:90) at a GCE in BR buffers at pH 2, 3, 4, 5, 6, 7, 8, 9, 10. The scan rate was 50 mV s⁻¹. The reference electrode was Ag/AgCl.

According to Nicholson (Bard, and Faulkner, 2001), for an irreversible anodic reaction, the relationship between $E_p$ and $\nu$ is described as follows:

$$E_p = E^0 + \frac{RT}{nF} \log\left(\frac{1-\alpha}{\alpha}\right) + \frac{nF\alpha}{RT} \log\left(\frac{D_1/2}{k_s}\right)$$

(1)

where $E^0$ is the formal standard potential, $\alpha$ is the charge transfer coefficient, $n_\alpha$ is the number of the electrons transferred in the rate determining step, $D$ is the diffusion coefficient of Furan, $k_s$ is the standard heterogeneous reaction rate constant, $F$, $R$, and $T$ have their usual meaning. Thus the value of $(1-\alpha)n_\alpha$ can be easily calculated from the slope of $E_p$ vs. log $\delta$. In this system, the slope is 0.149, taking $T = 298$ K, $R = 8.314$ J K⁻¹ mol⁻¹ and $F = 96,480$ C, $(1-\alpha)n_\alpha$ was calculated to be 0.2. Generally, the results suggested that one-electron transfer process are the rate-limiting by step.
Fig. 5. A: Cyclic voltammograms of 1mM furan solutions in methanol-water (10:90) in 0.1 M Britton-Rabinson buffer solution (pH=5), at various scan rates, from 25 to 250 mV/s. 
B: Variation of \( v^{1/2} \) with anodic peak current I, at a GCE with Ag/AgCl as reference electrode.

Fig. 6. A: Variation of the logarithm of peak current \( I \) with the logarithm of the scan rate. B: Variation of \( E_p \) versus the logarithm of the scan rate for 1mM Furan.
assuming charge transfer coefficient $\alpha = 0.8$ for Furan. Differential-pulse voltammetry (DPV) is one of the most sensitive electrochemical detection methods. Therefore, DPV was used for determination of Furan. Under the optimized experimental conditions, the DPV curves were obtained using different concentrations of Furan (Fig. 7A). As it can be seen, the height of the DPV peaks ($I_{pa}$) increases with increase in concentration of Furan. The calibration curve was obtained using data from these measurements (Fig. 7B). According to the obtained results, linear calibration graphs were obtained for Furan with the linear dynamic range of 12–360 $\mu$M (0.81–24.5 ppm). The linear regression equations were $I_{pa} (\mu A)=2.063+0.024C_{\text{Furan}} (\mu M)$, with a correlation coefficient of 0.999 and a sensitivity of 0.024 $\mu$A/\mu M. A limit of detection (LOD) of 3 $\mu$M (0.68 ppm) were calculated according to the 3 $s_b$/m and 10 $s_b$/m criterions, respectively, where m is the slope value of the calibration curve and $s_b$ is the calculated standard deviation for the peak currents of the blank (Four runs).

The reproducibility of the method was tested by analyzing 10 samples containing 30 $\mu$M of Furan. The RSD % of the method thus obtained was 3.0 % which showed excellent reproducibility for this developed methods. To demonstrate the efficiency of the method, the developed method was applied for determination of Furan in three different beverage samples. The recovery experiments were carried out using the standard addition method by adding the known amounts of Furan to the beverage samples, and the calibration plot was used for determination of spiked Furan in beveragesamples. The results of recovery

<table>
<thead>
<tr>
<th>Beverage</th>
<th>Spiked ($10^{-6}$M)</th>
<th>Found ($10^{-6}$M)</th>
<th>Recovery(%) + RSD%</th>
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<tr>
<td>Sample 1</td>
<td>30</td>
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<tr>
<td></td>
<td>70</td>
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<td>98.7 ± 4.2</td>
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<tr>
<td>Sample 2</td>
<td>30</td>
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<td>103 ± 4.1</td>
</tr>
<tr>
<td></td>
<td>50</td>
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<td>101.6 ± 3.2</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>68.7</td>
<td>98.14 ± 3.6</td>
</tr>
<tr>
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<td>96.6 ± 3.2</td>
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<tr>
<td></td>
<td>70</td>
<td>68.2</td>
<td>97.4 ± 4.7</td>
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a: four determination
experiments were also shown in Table1. The results illustrated that the proposed method is accurate enough for practical applications.

CONCLUSION
A glassy carbon electrode was used as the working electrode for determination of Furann. The electrocatalytic activity of the GCE electrodes showed a good electro-catalyst effect toward Furann electro-oxidation. The results of oxidation kinetics of Furann indicated that the oxidation process is diffusion controlled. Finally, the oxidation current of Furann on GCE electrodes was used for determination of Furann in aqueous solution and a linear calibration was found in the range of 12-360 µM. Therefore this method can be used for quantitative determination of Furann in real samples.

REFERENCES


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Furan in Beverage


