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Voltammetric Determination of Triclosan in Waste Water and Personal Care Products

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An analytical method based on the effect of surfactant on the voltammetric behavior of triclosan was developed, optimized and validated for the determination of trace amount of triclosan. Based on increasing the oxidation current of triclosan in the presence of sodium dodecyl sulfate, a voltammetric technique for determining triclosan is proposed. The calibration curve is linear with two linear ranges of 10-600 µg L^{-1} and 1-8 mg L^{-1}. The limit of detection was obtained as 5µg L^{-1} and relative standard deviation was lower than 4.5 %. The method was successfully applied to analyze wastewater and personal care products samples.

Keywords: Determination, triclosan, surfactant, voltammetry

1. INTRODUCTION

Triclosan (2,4,4'-trichloro-2'-hydroxydiphenylether, Irgasan, TCN), a chemical used for its antibacterial properties, is an ingredient in many detergents, dish-washing liquids, soaps, deodorants, cosmetics, lotions, anti-microbial creams, various toothpastes and an additive in various plastics and textiles [1].

As a consumer product ingredient, the majority of TCN enters sewer system and is transported to wastewater sewage treatment plants. Once in the aquatic environment, TCN can undergo a series of transformation reactions to produce, in some cases, more toxic or bio-accumulative compounds [2, 3]. These reactions lead to the formation of compounds such as 2, 8-dichlorodibenzo-p-dioxin, chlorinated dioxins and dichloro and trichlorophenols [4]. It was also reported that TCN is toxic to aquatic living

organisms such as fish, daphnia magna and in particular to algae, for which its presence in environment has serious implications on the resistance mechanisms of bacteria [2]. Therefore, the safety of triclosan has been questioned in regard to environmental and human health. While the companies that manufacture products containing this chemical claim that it is safe, the United States Environmental Protection Agency (EPA) has registered it as a pesticide. The EPA gives triclosan high scores both as a human health risk and as an environmental risk.

Thus, the qualitative analysis of TCN is an important factor to monitor it in environmental and biological metrics as well as in commercial formulations. Up till now many reports have been focused on this topic and a great deal of analytical methods have been developed including liquid chromatography with diode array [5] gas chromatography coupled to mass spectrometry(GC-MS) [6], liquid chromatography-mass spectrometry (LC-MS) [7] and solid-phase micro extraction [8]. These methods require expensive instrumentation, which may not be available in many laboratories. Also, analysis time is long, detection limit is sometimes poor and in some cases special pretreatment is required before analysis. To the best of our knowledge there are few reports of electrochemical behavior of TCN at a screen-printed carbon electrode [9], on mercury electrode [10, 11], chemically surface-modified carbon nanoparticle [12,13] and on film composed of carbon-nanoparticles [14-17]. Phani K.L.N. et al. [18] reported the voltammetric detection of TCN based on hydrotrope-driven disruption of micellar encapsulates for complete release of TCN in the analyte solution. The present work describes a very simple, rapid and sensitive voltammetric method for the trace determination of TCN by inclusion of TCN within polymeric micelles to enhance water-solubilization and bioavailability of this poorly water soluble drug.

2. EXPERIMENTAL

2.1. Reagents and Chemicals

Triclosan was obtained from the Ciba Specialty Chemical Int. with a purity of minimum 99%. Stock solutions of triclosan were prepared by dissolving the solid in minimum amount of NaOH and diluting with water. A stock Britton-Robinson (B-R) buffer solution 0.04 M with respect to boric, orthophosphoric and acetic acid was used to control the pH of solutions tested. All chemicals were of analytical-reagent grade and used without further purification. Doubly distilled deionized water was used throughout.

2.2. Apparatus

Electrochemical measurements were carried out with Metrohm model 746VA trace analyzer connected to a 747 VA stand. The working electrode was a glassy carbon rod (2 mm diameter). Before use the working electrode was sequentially polished with graded 10 μM alumina powder, and rinsed with doubly distilled water. A platinum wire and a commercial Ag/AgCl, 3M KCl from Metrohm were used as an auxiliary and reference electrodes respectively. The scan rate in cyclic voltammetry was 100

mVs^{-1}, with exception of the experiments in which the influence of this variable was studied. The pulse height and scan rate at differential pulse voltammetry were 50 mV and 50 mVs^{-1}, respectively. All solutions were purged with pure nitrogen for 10min before the voltammetric runs.

2.3. General Procedure

A certain volume of pH 3.0 B-R buffer solutions was added into an electrochemical cell, then a measured-volume TCN solution and 10.0 mg L^{-1} sodium dodecyl sulfate (SDS) were added into the cell, and it was accumulated for 20 min under open-circuit. Then the voltammograms were recorded in a positive direction from 0.0 to 1.1 V. The change in current (increase of the current) at a potential in the range 0.4 to 1.1 V was measured as the analytical signal.

2.4. Procedure for Analysis of Real Samples

A suitable amount of the personal care products sample was weighed and dissolved in 1 ml sodium hydroxide and dilute with water (100 ml). The separation of other organic materials could be performed by three 25 ml portions of chloroform. One milliliter of the aqueous solution was transferred to a 10 ml solution of B-R buffer (pH 3) containing 10.0 mg L^{-1} SDS for determination. Exactly similar procedure was applied to the determination of TCN in wastewater by taking an appropriate volume of wastewater sample without any pretreatment.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of TCN

Initial differential pulse voltammetric studies were performed on TCN in various pH of B-R buffer at glassy carbon electrode. As it is shown in Fig.1 a well-defined anodic peak due to the oxidation at the phenolic moiety was observed [9] which its potential is shifted to less positive values by increasing pH.

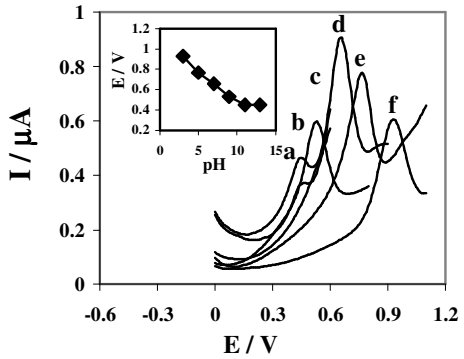

Figure 1. The differential pulse voltammograms of 1 mg L^{-1} TCN at various pH of B-R buffer on glassy carbon electrode, pH: (a) 13, (b) 11, (c) 9, (d) 7, (e) 5, (f) 3. Inset, the plot of E vs. pH.

Fig. 1, inset shows a plot of E vs. pH and the break point indicates a pK_a value of about 7.9, which agrees well with the literature value [19]. The effect of scan rate on the peak current was examined between 100 to 600 mVs^{-1}.

The linearity of current vs. $\upsilon^{1/2}$ demonstrating a diffusion-controlled process. Adsorption phenomena can also be identified by the effect of accumulation potential prior to scanning the potential. It was found that preconcetration potential slightly affected the peak current. However, the current is increased under open-circuit for 20 min in the solution of TCN before carrying out voltammetric examinations.

3.2. The Effect of surfactant

TCN is a synthetic broad spectrum antibacterial agent with a phenolic chlorinated polyromatic hydrocarbon structure [20]. The main hurdle in the development of effective formulations is, as in the case of more than 50% of the drugs approved for use, the lower solubility of TCN in aqueous media [21]. TCN is significantly soluble in water only as anion at sufficiently alkaline pH. The oxidation of TCN at electrode surface is facile but highly irreversible and usually associated with the formation of an insulating polymeric blocking film [14]. Phani and coworkers [18] have reported that the peak current height of TCN at concentration range of 0.2 to 1.0 mM is decreased at basic medium (pH 11) with exposing electrode to a solution containing surfactant for about 60 min. However we found that at acidic pH and lower concentration range as the surfactant concentration was increased, the peak height was increased. As it is shown in Fig. 2, the peak height of 1 mg L^{-1} of TCN is increased under open-circuit in the solution of 10 mg L^{-1} SDS (pH 3) for 20 min while the peak current of 150 mg L^{-1} TCN at pH 11 is decreased under the same condition which was reported previously[4] (Fig. 2, inset). The effect of surfactant on the anodic peak current was examined by either adding the various surfactants (hexadecyltrimethylammonium bromid, N-cetyl-N,N,N-triethylammoniumbromid and Triton-X100) at acidic pH.

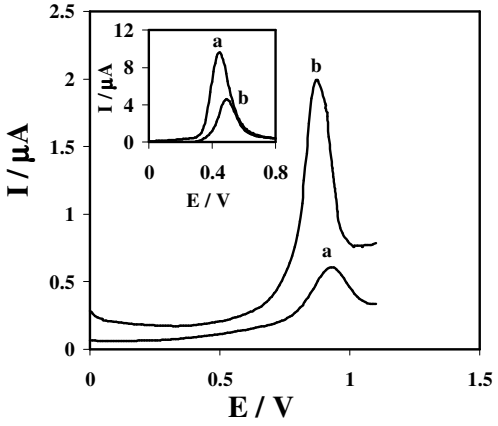

Figure 2. (a) The differential pulse voltammogram of 1 mg L^{-1} TCN at pH 3 of B-R buffer in the absence of SDS, (b) in the presence of 10 mg L^{-1} SDS. Inset, (a)The differential pulse voltammograms of 150 mg L^{-1} TCN at pH 11 of B-R buffer in the absence of SDS, (b) in the presence of 0.02% W/W SDS.

The results show that the peak current increases in the presence of all the surfactants and the more obvious increase was observed for SDS; that is considered in our experiments. The reason of increase of the current in the presence of SDS could be due to the anti-fouling effect of SDS. Hoyer et al. [22] reported the effect of SDS in suppressing electrode fouling by bioorganic compounds at glassy carbon electrode. The anti-fouling effect is enhanced by the fact that SDS forms soluble aggregate with several types of surface-active compounds including proteins and hydrophilic polymers [23] and these compounds are thus scavenged by SDS. They reported that the strength of interaction with surfactants generally increases in the order nonionic surfactant<< cationic surfactants<< SDS, which is in good agreement with our observed results.

3.3. The Effect of SDS Concentration

The concentration of SDS also affects the peak current. The oxidation peak current increases during the SDS concentration from 0.0 to 7.0 mg L^{-1}, then keeps stable with increasing concentration (Fig . 3). In the experimental, the SDS concentration is 10 mg L^{-1}.

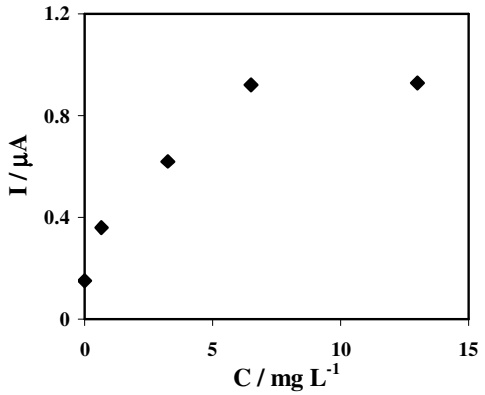

Figure 3. The relationships between peak current and concentration of SDS.600 μg L^{-1}, pH 3 B-R buffer solution, accumulation time 20min.

3.4. Accumulation Potential and Time

The effects of accumulation potential on the oxidation peak current were investigated. When the accumulation potential shifts from 0.0 to 0.5 V, the oxidation peak current alters very slightly. This reveals that the accumulation potential has no obvious influence on the oxidation current of TCN under this conditions.

In this experiment, the accumulation was carried out under open-circuit. The influences of accumulation time on the peak current are shown in Fig 4. The peak current increases linearly with the accumulation time in the range of 0-20 min. However, the peak current does not increase as further increasing accumulation time when the accumulation time beyond 20 min. This may be due to the

adsorption of TCN at the electrode surface tends to become saturation. Normally, the optimum of accumulation time was selected as 20 min.

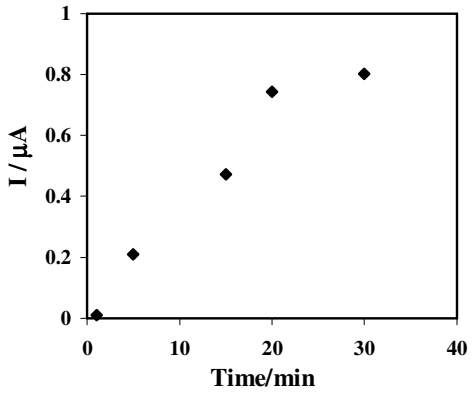

Figure 4. The effect of accumulation time on peak current of 600 μg L^{-1} TCN in the presence of 10 mg L of SDS.

3.5. The Effect of Ionic Strength

The effect of ionic strength of the TCN solution on the anodic peak current was examined by varying the concentration of $NaNO_3$ up to 1.0 M. The results showed that the change of ionic strength did not have any effect on peak current response.

3.6. The Effect of pH in the Presence of SDS

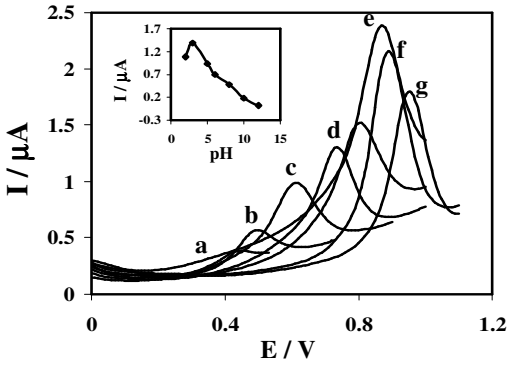

Figure 5. The differential pulse voltammograms of 1 mg L^{-1} TCN in the presence of 10 mg L^{-1} SDS at various pH of B-R buffer on glassy carbon electrode, pH: (a) 12, (b) 10, (c) 8, (d) 6, (e) 5, (f) 3, (g) 2. Inset, the plot of I vs. pH.

The effect of pH on the anodic peak current of TCN in the presence of SDS was examined by differential pulse voltammetry and the results are shown in Fig. 5.

Again by increasing pH the potential is shifted to less positive potential. The optimum pH was selected for maximum sensitivity and obtained well-defined base current. It was observed that peak current reached a maximum at pH value 3 and decreased after that (Fig. 5, inset).

3.7. Analytical Application, Analytical Figures of Merit

The relationship between the variation in the best current and TCN concentration was found to be linear over two limited concentration ranges. Under the optimum conditions, calibration cure shows two dynamic linear range of 10 to 600 μg $L^{-1}$and 1 to 8 mg L^{-1} (Fig. 6). The limit of detection (LOD),was obtained as $Y_{LOD}=X_B+ 3S_B$, where Y_{LOD} is the signal for limit of detection, X_B and $3S_B$ are the mean and the standard deviation of the blank signal, respectively [24] (table 1). Under optimum experimental conditions the limit of detection (LOD) was obtained as 5 μg L^{-1}.

Table 1. The equations for calibration curves

Entry	Equation	Linear range /μg L^{-1}	r	LOD μg L^{-1}	Recovery (%)	R.S.D.(%) (n=10)
1	Y=0.2985x + 1.030	10-600	0.997	5	94.1	4.45
2	Y=1.0653x – 0.003	1000-8000	0.978	-	90.2	4.14

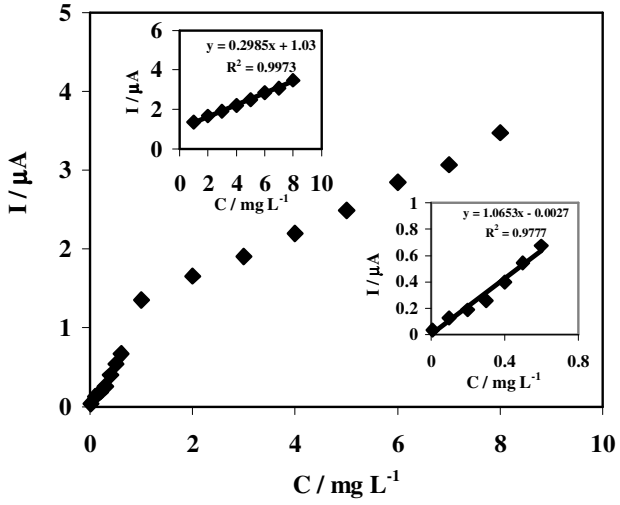

Figure 6. The plot of voltammetric peak current of TCN in the presence of 10 mg L^{-1} SDS ratio in aqueous 0.04 M B-R buffer pH 3. Inset, right-bottom, the linear dynamic range of 10 to 600 □g L^{-1} TCN. Inset, left-up, the linear dynamic range of 1000 to 8000 μg L^{-1} TCN.

The reproducibility of the method was checked by successive determinations (n=10) of TCN in the two concentration ranges. The relative standard deviations (R.S.D.) were lower than 4.5 %.

3.8. Interferences

The surface active materials such as hexadecyltrimethyl and Triton X-100 have no effect on the signal at the ratio 5:1 of interfere/TCN. The possible interferences of several metal ions such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Al^{3+}, Cr^{3+}, Pb^{2+}, Mn^{2+}, Sn^{2+}, Fe^{3+}, Co^{2+} and Zn^{2+} were investigated. Only Zn^{2+} and Co^{2+} were interference at 1:2 and 1:5, respectively.

3.9. Application to Real Matrices

To evaluate the applicability of the present methodology on real matrices, assays were performed in commercial toothpaste, hand gel, liquid soap and wastewater. The results showed that satisfactory recovery for TCN could be obtained (table 2) using the recommended procedure. Table 2 resumes the data obtained for TCN assays performed on the matrices studied using the optimized experimental methodology.

Table 2. Results of analysis of real samples

Sample	Added[a] $\mu g\ L^{-1}$	Found[a] $\mu g\ L^{-1}$	Actual Concentration in Real sample (%)	Recovery (%)	R.S.D. (%)
Toothpaste	-	88.8	0.29	-	-
	100	179.7	0.28	98	4.2(n=4)
Hand gel	-	60.2	0.20	-	-
	120	169.3	0.18	94	3.8(n=4)
Liquid soap	-	64.3	0.21	-	-
	60	105.1	0.18	85	4.2(n=3)
Wastewater	-	0.014	-	-	-
	0.1	0.103	-	90	2.8(n=3)

4. CONCLUSIONS

The present procedure offers the opportunity of a simple, rapid practical and reliable methodology for the determination of TCN in aqueous media. Parameters affecting the procedure were fully discussed. Under optimized experimental conditions a good analytical performance was attained, including suitable precision, excellent linear dynamic range and detection limits at the trace level. The application of the present analytical approach to commercial toothpaste and wastewater matrices

demonstrated remarkable selectivity, sensitivity and accuracy. Besides the present methodology has proved to be a convenient tool to monitor TCN at the trace level in real samples.

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