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Electroanalytical method for the determination of methylparaben

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ABSTRACT

A gold electrode (GE) was used for the electroanalytical determination of methylparaben in a pharmaceutical product and urine sample by cyclic, linear sweep and square-wave voltammetric techniques. The oxidation of methylparaben is irreversible and exhibits a diffusion controlled process. The oxidation mechanism was proposed. The dependence of the current on pH, the concentration and scan rate was investigated to optimize the experimental conditions for the determination of methylparaben. It was found that the optimum buffer for the determination of methylparaben is pH of 7.0, a physiological pH. In the range of 0.04 to 1.00 mM, the current measured by square wave voltammetry presents a good linear property as a function of the concentration of methylparaben with limit of detection 1.71 μM and limit of quantification 5.70 μM. In addition, the reproducibility (RSD of 1.06%), precision (RSD of 1.27%) and accuracy (98.05–103.4%) of the method were checked as well. Electroanalytical determination of methylparaben in pharmaceutical products and urine was done using only square wave voltammetry. The method finds its applications in quality control laboratories.

1. Introduction

Preservatives are often added to pharmaceutical and cosmetic formulations to manage microbial contamination. Alkyl esteres of *p*-hydroxybenzoic acid (parabens) are the most widely employed preservatives in cosmetic products due to their broad antimicrobial spectrum and effectiveness. The most common parabens used in cosmetic products are methylparaben (MePa) (Scheme 1), ethylparaben (EtPa), propylparaben (PrPa) and butylparaben (BuPa). They are often used in combination, since they have synergetic effects in a wide variety of products such as cosmetics, ointments and suspensions [1–3], which allows the use of lower levels while increasing preservative activity. Parabens have multiple biological actions, but it is generally related that their inhibitory effects on membrane transport and mitochondrial function processes are keys for their actions [1].

Since the presence of parabens was detected in human breast tumors by Darbre [4,5], the use of these preservatives in cosmetics has been discussed worldwide. It was also reported that parabens have estrogenic activity, since the compounds have been shown to bind to estrogen receptors from different sources. The use of parabens in cosmetic products as a preservative is permitted in several countries, up to a maximum concentration of 0.4% (w/w) in the finished product for one ester and up to 0.8% (w/w) for mixtures of esters expressed as p-hydroxybenzoic acid [6].

Several analytical methods have been reported for the determination of parabens in a variety of matrices, among others, high performance liquid chromatography (HPLC) [2,3,7], reverse phase high performance liquid chromatography [8] and capillary electrophoresis [9], micellar electrokinetic chromatography and mass spectrometry [10]. A few electroanalytical methods have been reported for the determination of parabens [11–14]. Electrochemical methods may offer certain advantages, such as requiring easier sample preparation, being less time-consuming and offering detectivity and dynamic range comparable to other analytical methods [15,16]. These methods have proven to be useful for development of very sensitive and selective methods for the determination of organic molecules including drugs and related molecules in pharmaceutical dosage forms and biological fluids [17].

Electrochemical method especially, square wave voltammetry (SWV) makes it possible to decrease the analysis time as compared to the time exhausted by chromatographic methods [18]. The advantage of SWV is that a response can be found at a high effective scan rate, thus reducing the scan time. For this reason SWV is employed more often than normal pulse voltammetry (NPV) and differential pulse voltammetry (DPV) techniques. There are other advantages: greater speed in analysis and lower consumption of electroactive compounds in relation to DPV, and reduced problems with blocking of the electrode surface.

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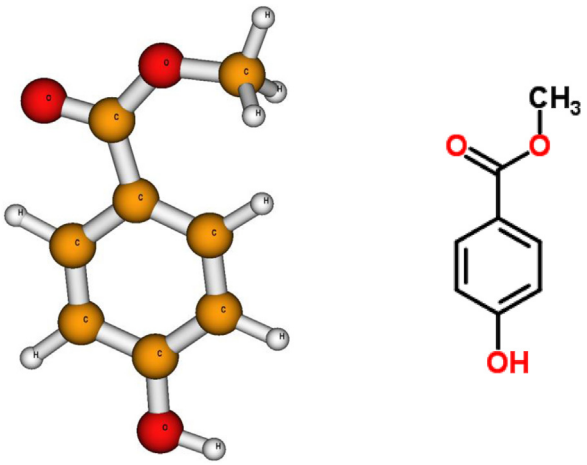

Scheme 1. Chemical structure of methylparaben.

To our knowledge, the electroanalytical method for the determination of methylparaben using gold electrode has not been reported yet. The aim of this study is to establish the suitable experimental conditions, to investigate the voltammetric behavior and oxidation mechanism of methylparaben at gold electrode by cyclic, linear sweep and square wave voltammetric methods for the direct determination of methylparaben in real samples like pharmaceuticals and urine.

2. Experimental

2.1. Reagents and chemicals

Methylparaben was obtained from Sigma Aldrich and used without further purification. A stock solution of methylparaben (1.0 mM) was prepared in methanol and stored in a refrigerator at 4 °C. Standard working solutions were prepared by diluting the stock solution with the selected supporting electrolyte. The phosphate buffers from pH 3.0–10.4 were prepared according to the method of Christian and Purdy [19]. The pharmaceutical products containing methylparaben were purchased from a local pharmacy in India. Other reagents used were of analytical grade. All solutions were prepared with Millipore water.

2.2. Instrumentation

Electrochemical measurements were carried on a CHI 630D electrochemical analyzer (CH Instruments Inc., USA). The voltammetric measurements were obtained in a 10 mL single compartment three-electrode glass cell with Ag/AgCl, (3 M KCl) as a reference electrode, a platinum wire as counter electrode and a 2.0 mm diameter gold electrode as a working electrode (Part No. CHI101). pH measurements were performed with Elico LI120 pH meter (Elico Ltd., India). All experiments were carried at an ambient temperature of 25 ± 0.1 °C.

The area of the electrode was obtained by the cyclic voltammetric method using 10.0 mM $K_3Fe(CN)_6$ as a probe at different scan rates. For a reversible process, the following Randles–Sevcik formula [20] can be used.

$$I_{pa} = 0.4463\left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A_0 D_0^{1/2} C_0 \upsilon^{1/2} \quad (1)$$

where, I_{pa} refers to the anodic peak current, n is the number of electrons transferred, A_0 is the surface area of the electrode, D_0 is diffusion coefficient, υ is the scan rate and C_0 is the concentration of $K_3Fe(CN)_6$, respectively. For 10.0 mM $K_3Fe(CN)_6$ in 0.1 M KCl electrolyte, $T = 298$ K, $R = 8.314$ J K^{-1} mol^{-1}, $F = 96{,}480$ C mol^{-1}, $n = 1$, $D_0 = 7.6 \times 10^{-6}$ cm^2 s^{-1}, [21] then from the slope of the plot of I_{pa} vs. $\upsilon^{1/2}$, the electrode surface area was calculated. In our experiment the slope was 2×10^{-5} μA (V s^{-1})$^{-1/2}$ and the area of electrode were calculated to be 0.0269 cm^2.

2.3. Analytical procedure

The polishing was done on micro cloths (Buehler) glued to flat mirrors. The particle size was 0.05 μm. After initial cleaning of the electrode, it was only necessary to polish with 0.05 μm particle size without any time consuming during the experiments. The polishing procedure is also easier and efficient than the glassy carbon electrode. Before transferring the electrode to the solution, it was washed with double distilled water. Cyclic voltammograms were recorded in phosphate buffer of pH = 7.0 with ionic strength 0.2 M at 50 mV s^{-1} between 0.00 to 1.40 V, until obtaining the reproducible current–potential curves.

The parameters for Linear sweep voltammetry (LSV) and square wave voltammetry (SWV) were initial potential: 0.00 V; final potential: 1.40; increase potential: 0.004 V; amplitude: 0.05 V; frequency: 15 Hz; quiet time: 2 s; sensitivity: 1×10^{-5} A/V.

2.4. Sample preparation

For the cosmetic samples, a mass equivalent to a methylparaben stock solution of a concentration of about 1.0 mM was accurately weighed and dissolved in methanol. The content of the flask were sonicated for 20 min until complete dissolution. The excipient was separated by filtration. The filtrate was transferred into a 100 mL calibrated flask and diluted to a final volume with methanol. Appropriate solutions were prepared by taking suitable aliquots from this stock solution and diluting them with the phosphate buffer solutions. A required amount of this solution was then transferred to a voltammetric cell and SWV voltammograms were recorded. The nominal content of methylparaben in cosmetic samples was determined either from the analytical curve or from the corresponding linear equation.

3. Results and discussion

3.1. Cyclic voltammetric behavior of methylparaben

The electrochemical behavior of methylparaben at gold electrode was investigated using cyclic voltammetry (CV) at physiological pH = 7.0. The cyclic voltammograms obtained for 1.0 mM methylparaben solution at a scan rate of 50 mV s^{-1} exhibits a well-defined irreversible anodic peak at about 0.929 V at gold electrode. The results are shown in Fig. 1. The cathodic peak that appeared was corresponding to the reduction of gold oxides as exhibited in earlier works [22].

3.2. Influence of pH

The electrode reaction might be affected by pH of the medium. The electro-oxidation of 1.0 mM methylparaben was studied over the pH range of 3.0–10.4 in phosphate buffer solution by cyclic voltammetry. Since well-defined oxidation peaks appeared between pH 3.0 and 10.4 (Fig. 2A). With the increase in pH of the solution, the peak potential linearly shifted to less positive values and the linear relation between E_p and pH (inset plot of Fig. 2A) can be expressed as:

$$E_p = 1.370 - 0.0620\,\text{pH}; \quad r = 0.9910.$$