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A novel method based on electrochemical approaches and multivariate calibrations for study and determination of methylparaben in the presence of unexpected interference in cosmetics

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ABSTRACT

The use of multivariate voltammetric calibration for the simultaneous determination of two preservatives (methylparaben (MP) and propylparaben (PP)) in cosmetics is reported. At first, electrochemical studies of MP and PP were done by cyclic voltammetry (CV), chronocoulometry (CHC) and linear sweep voltammetry (LSV) techniques. Then central composite rotatable design (CCRD) and response surface methodology (RSM) were used for simultaneous optimization of effective parameters on voltammetric responses of the two analytes. The optimum values of pH, scan rate, step potential and pulse height were 7.0, 0.062 V s^{-1}, 0.009 V and 0.07 V, respectively. After optimization, the resolution of the two multicomponent mixtures has been accomplished by partial least squares (PLS) for voltammmetric studies of them at the surface of a glassy carbon electrode. Finally, the proposed method was found to be applicable for routine analysis (recovery tests) of the preservatives in a cosmetic product.

1. Introduction

One of the fundamental problems in analytical chemistry is the simultaneous determination of compounds in real samples. The development of chemometric methods, namely classical least square (CLS), inverse least squares (ILS), principal component regression (PCR) and partial least squares (PLS) has solved, many problems of the simultaneous analysis of multi-mixtures containing two or more compounds [1–4]. Comparing to other conventional techniques, chemometric methods do not apply any pretreatment such as the separation procedure in chromatography, a division of the spectrum in ratio spectra derivative spectrophotometry and a derivation of spectrum in derivative spectrophometry. However, the separation of overlapped peaks is essential for simultaneous determinations in every area of analytical science.

Parabens are alkyl esters of p-hydroxybenzoic acid that have been used as preservatives for over 70 years in the pharmaceutical, food and cosmetic industries due to their broad antimicrobial spectra, low toxicity and low price [5]. Methylparaben (MP), methyl 4-hydroxybenzoate, and propylparaben (PP), propyl 4-hydroxybenzoate (Scheme 1) are the most commonly applied parabens and are often used together since they have synergistic effects [6]. It had been found that the antimicrobial effects of the parabens seem to increase with increasing chain length. However, esters of longer alkyl chains are of limited applications due to their lower solubility in water [7].

There are a great number of publications describing various methods for the determination of MP and PP preservatives separately or in combination with other drugs by HPLC and other techniques [8–10]. These techniques need expensive instrumentation with high operating costs and sample extraction and are time-consuming. Also electrochemical detection has been used in connection to capillary zone electrophoresis (CZE) and high performance liquid chromatography (HPLC) [11–13] but scarce examples of simple electroanalysis of parabens have been reported to date [14,15].

In this contribution we reported study and simultaneous determination of MP and PP by electrochemical techniques and multivariate calibrations at the surface of a glassy carbon electrode (GCE). For this purpose, a strategy based on central composite rotatable design (CCRD) and response surface methodology (RSM)

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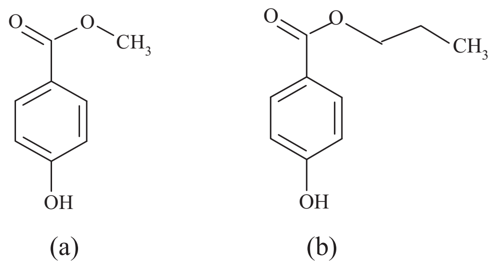

Scheme 1. Structures of (a) methylparaben and (b) propylparaben.

has been applied not only to accomplish a systematic study but also to prove the interesting possibilities of the methodology in voltammetric studies.

2. Experimental

2.1. Apparatus and electrodes

Electrochemical experiments were carried out with a Sama 500 potentiostat (Isfahan, Iran) using a conventional three-electrode configuration. An Ag/AgCl/KCl 3.0 M (Metrohm), a platinum wire (Metrohm, Switzerland) and a GCE (Metrohm, Switzerland, diameter, 1 mm) were employed as reference, counter and working electrode, respectively. All measured potentials were referred to this electrode system. A model 691 pH meter (Metrohm, Switzerland) was applied to adjust the pH of the buffer solution, which was used as the supporting electrolyte in the electrochemical experiments. Deionized water was produced from an ultrapure water system (smart 2 pure, TKA, Germany).

2.2. Reagents

MP, PP, phosphoric acid, sodium hydroxide and other chemicals were purchased from Merck and used without any further purification. The diluted standard solutions were prepared daily. The reagents used throughout were analytical grade and aqueous solutions were prepared in deionized water at 25 ± 0.5 °C. All electrochemical measurements were conducted in 0.2 M phosphate buffer solution (PBS), pH 7.0.

2.3. Experimental design

The most effective factors on the performance differential pulse voltammetry (DPV) measurements, including the scan rate (X_1), step potential (X_2) and pulse height (X_3), were chosen based on literature and preliminary experiments. In order to optimize the values of these parameters and to reach the best response, CCRD was used. CCRD, which is one of the most frequently used RSM, is affected by a combination of several parameters. RSM plays an important role in designing, developing and analyzing new scientific research, as well as improving existing studies and products.

The number of experiments (n) based on CCRD consisted of $n = 2^f + 2f + r$ runs, where f is the number of factors, 2^f is the number of the factorial points at the corners of the cube, $2f$ is the number of the axial points on the axis of each design factor at a distance of $\pm\alpha$ ($\alpha = \pm 2^{f/4} = 1.68$ for $f = 3$) from the center of the cube, and r is the number of the replication of center points at the center of the cube. Center point is replicated to find the experimental error [16]. Accordingly, the total number of experiments in the present work for $r = 3$, was $8 + 6 + 3 = 17$.

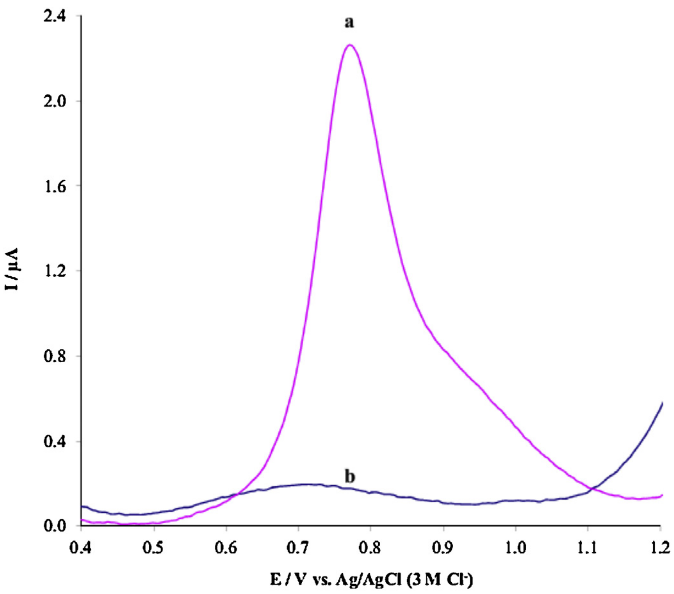

Fig. 1. (a): Differential pulse voltammogram of GCE in 0.2 M PBS (pH = 7.0), and (b): (a) +200.0 µM of MP and PP. Scan rate: 100.0 mV s^{-1}.

The mathematical relationship of Y response (peak current of differential pulse voltammograms) on the corresponding factors is expressed by the second-order polynomial equation (Eq. 1):

$$\begin{aligned}Y = {} & \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_5X_5 + \beta_{11}X_1^2 + \beta_{22}X_2^2 \\ & + \beta_{33}X_3^2 + \beta_{44}X_4^2 + \beta_{55}X_5^2 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{14}X_1X_4 \\ & + \beta_{15}X_1X_5 + \beta_{23}X_2X_3 + \beta_{24}X_2X_4 + \beta_{25}X_2X_5 + \beta_{34}X_3X_4 \\ & + \beta_{35}X_3X_5 + \beta_{45}X_4X_5 \qquad (1)\end{aligned}$$

where Y is the predicted response, X_i is the independent variables, β_0 is intercept (constant), β_i, β_{ii} and β_{ij} are the linear, quadratic and interaction coefficients, respectively.

According to the design, each of the three factors (X_1, X_2 and X_3) was studied at five levels (Table 1). MINITAB® Release 16, developed by Minitab Inc. (USA), a statistical software package, was applied for data processing and studying linear terms, squared terms and interaction between the factors. The significance level 95% was set for the mathematical model and surface response.

2.4. Multivariate calibration

A calibration set of 25 samples was prepared in 0.2 M PBS. PLS and PCR models were applied to the differential pulse voltammograms of these mixtures. For analyzing of MP and PP in cosmetic products, Himalaya cream (GCSCIL.L.C, Dubai) was used and a calibration set of 7 samples organized. The stock solution was prepared in ethanol-deionized water (50:50) mixture.

3. Results and discussion

3.1. Oxidation of MP and PP on the glassy carbon electrode

The electrochemical behaviors of MP and PP at GCE have been investigated by DPV. Fig. 1 shows the DPV responses for the electrochemical oxidation of 200.0 µM MP and PP at the surface of a GCE at scan rate of 100.0 mV s^{-1} in PBS (pH = 7.0). As can be seen, MP and PP show only one peak in DPV. Thus for simultaneous determination of MP and PP it is necessary to resolve their peaks. For achieving the purpose chemometric methods was coupled with voltammetry.