

## Determination of Hydroquinone in a Square Wave Voltammetry Based on Screen Printed Carbon Electrode

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### ABSTRACT

Hydroquinone is a phenolic compound are often used extensively in the cosmetics industry as whitening agent. This compound is very toxic and their use should be monitored. Due to the impact of hydroquinone, the use of hydroquinone restricted by BPOM (Food and Drug Regulatory Department in Indonesia) maximum by 0.02%. The aim of this study was to establish a new simple sensitive voltammetry method for determination of hydroquinone using screen printed carbon electrode (spce). In this study, linear concentration range, limit of detection, sensitivity and accuracy were investigated. Before the determination of parameters analysis, the method require the optimization of method parameters such as frequency and pulse height. This study were showed that the measurement of hydroquinone with square wave voltammetry method has linear concentration range 1 - 100 $\mu$ M, limit of detection 23.4 $\mu$ M, sensitivity 0.075 $\mu$ M/ $\mu$ A and accuracy 0.9969. The proposed method was succesfully applied in whitening cream cosmetic samples with good enough results.

Key word: hydroquinone, spce, square wave voltammetry

### INTRODUCTION

Hydroquinone is a phenolic compound are often used extensively in the pharmaceutical, photography and cosmetics industry [1, 2]. The use of hydroquinone in cosmetics have a negative effect on the body [2] such as irritation and scars for a long-term use [3]. Due to the impact of hydroquinone, the use of hydroquinone restricted by BPOM (Food and Drug Regulatory Department in Indonesia) maximum by 0.02% [4]. However, there are still many whitening creams that are not labeled and circulate without permission, thus suspected containing hydroquinone. Therefore, this condition requires strict control and sensitive method.

Numerous methods have been developed for determining hydroquinone, including colorimetry, gas chromatography, HPLC, chemiluminescence, spectrophotometry and pH based-flow injection analysis [5]. While chromatography methods is a good option for the determination of hydroquinone, the procedure are time-consuming and requires complicated pretreatment. Due to the high sensitivity, rapid analysis and simple pretreatment [6], electrochemical method has been widely used in the determination of hydroquinone [5, 7, 8]. However, some of the previous methods often involves modification of electrode that require complicated procedure and the use of conventional electrode require large volume of analyte.

Square wave voltammetry is one of the most advanced electrochemical method in the recent years [9]. The most advantages of this method is the rapid analysis compared to the

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differential pulse voltammetry [10]. The peak current in this method is proportional to the concentration of the target analyte. This technique has very low detection limit reached  $1 \times 10^{-8}$  M [10].

The aim of this study was to establish a new simple sensitive voltammetry method for determination of hydroquinone. In this study, linear concentration range, limit of detection, sensitivity and accuracy were investigated. Before the determination of detection limit, the method requires the optimization of method parameters such as frequency and pulse height. The use of a screen printed carbon electrode (spce) provides the advantages of a small volume of analyte. The proposed method has been applied to determination of hydroquinone in real sample with good enough results.

## EXPERIMENT

### Chemicals and instrumentation

Hydroquinone was purchased from Merck. Phosphate buffer solution (0.1M) was prepared by mixing the stock solution of 0.1 M  $\text{H}_3\text{PO}_4$  and 0.1 M  $\text{KH}_2\text{PO}_4$ . Whitening cream cosmetic samples were purchased from a local cosmetics shop. All solutions were prepared with demineralized water and all the experiments were performed at room temperature.

Square Wave Voltammetric experiments were performed by Potentiostat/Galvanostat PG581 (Uniscan, England) with a personal computer. All experiments were carried out using a screen printed three electrode system consisting of the working carbon electrode, an Ag/AgCl as the reference electrode and a carbon as the auxiliary electrode. Screen printed electrodes were purchased from Quasense Inc., Thailand.

### Procedure

Voltammetry procedure involves three step experimental consist of optimization of method parameters, determination of limit of detection and determination of hydroquinone concentration in whitening cream sample. Optimization of method parameters consist of frequency and pulse height optimization. Frequency optimization performed with frequency variations 5–10 Hz with parameters as follow sweep potential -0.3–1.0 V, pulse height 0.1 V and current range 100  $\mu\text{A/V}$ . Pulse height optimization performed with pulse height variations 0.001 - 0.15 V with parameters as follow the sweep potential -0.3-1.0 V, frequency 10 Hz and current range 100  $\mu\text{A/V}$ . All the optimization experiments were carried out in the measurement of 1.0 mM HQ in 0.1M phosphate buffer (pH 2) as supporting electrolyte.

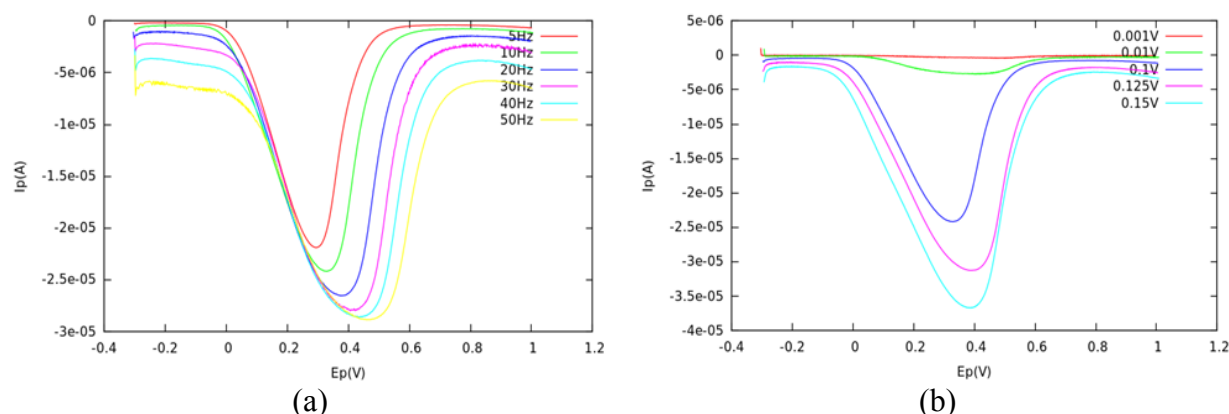
The determination of limit of detection were performed in an 0.1M phosphate buffer solution (pH 2) with varying concentration of HQ. The whitening cream sample were dissolved in the phosphate buffer solution (pH 2). Determination of hydroquinone concentration in whitening sample were done by standard addition technique. The square wave voltammogram were recorded with parameters as follow the sweep potential -0.3–1.0 V, frequency 10 Hz, pulse height 0.1 V and current range 100  $\mu\text{A/V}$ .

## RESULT AND DISCUSSION

### Optimization Parameters of Square Wave Voltammetry Method

The important parameters of this method were optimized before the determination of hydroquinone. The important parameters consist of frequency and pulse height. The optimization of frequency and pulse height were determined in measurement of 1.0 mM hydroquinone in 0.1 M phosphate buffer solution (pH 2). Figure 1a shows the relationship of frequency with peak current. The optimum frequency was obtained on 10 Hz. Figure 1b shows the relationship of pulse height with the peak current. The optimum pulse height was

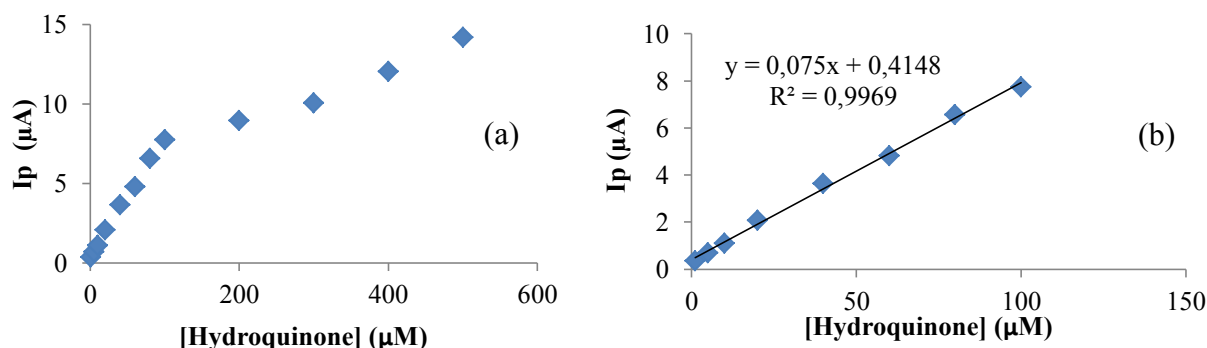
obtained on 0.1 V. The optimum frequency and pulse height were determined based on peak height and the smoothness of curve.



**Figure 1.** (a) The relationship of frequency with peak height (b) The relationship of pulse height with peak height

### Determination of Parameters Analysis

Parameter analysis include linear concentration range, limit of detection, sensitivity and accuracy were obtained from measurement the hydroquinone solution with concentration range 1-500  $\mu\text{M}$ . Figure 2(a) show the relationship of hydroquinone concentration with peak height. The linear concentration range were obtained from Figure 2 with the concentration range 1.0  $\mu\text{M}$  to 100  $\mu\text{M}$ . Figure 2(b) show the calibration curve of hydroquinone measurement. The sensitivity were obtained from the slope of regression equation  $I_p(\mu\text{A}) = 0.075[\text{Hydroquinone}] + 0.4148$ , the result is 0.075  $\mu\text{M}/\mu\text{A}$ . The accuracy were obtained from  $R^2$  is 0.9969. Limit of detection ( $S/N=3$ ) of hydroquinone measurement with square wave voltammetry is 23.4 $\mu\text{M}$ . This method show the rapid analysis time reaches 65 second per measurement. The limit of detection reflects that the proposed method is very sensitive to determine concentration of hydroquinone. The square wave voltammogram were recorded under optimized parameters.



**Figure 2.** (a) The relationship of hydroquinone concentration with peak height (b) The calibration curve of hydroquinone

### Application of the Method

The proposed method was applied to determine hydroquinone in whitening cream cosmetic samples. The results of the proposed method are shown in Table 1. For the analysis of hydroquinone in whitening cream sample, 5.0 g of sample was diluted to phospahte buffer

solution (pH 2), the filtrate was separated from the sediment and the filtrate was diluted to 100 mL with phosphate buffer solution (pH 2). The square wave voltammogram were recorded by standard addition technique under optimized parameters.

**Table 1.** The determination of hydroquinone concentration on whitening cream sample

Sample	[Hydroquinone] ( $\mu\text{M}$ )	%
A	21.75	0.024
B	10.31	0.011
C	0.480	0.001

## CONCLUSION

This study were showed that the measurement of hydroquinone with square wave voltammetry method has linear concentration range 1.0 – 100  $\mu\text{M}$ , limit of detection 23.4  $\mu\text{M}$ , sensitivity 0.075  $\mu\text{M}/\mu\text{A}$  and accuracy 0.9969. The proposed method was succesfully applied in whitening cream cosmetic samples with good results. The advantages of this method is easy, rapid analysis and simple because it does not requires complicated sample pretreatment.

## ACKNOWLEDGMENT

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