ELECTROCHEMICAL ANALYSIS OF BUTYLATED HYDROXYTOLUENE

Nur Anisa Rosyiidah and Pirim Setiarso*
Chemistry Department, Faculty of Mathematics and Natural Sciences, Surabaya State of University, Surabaya, Indonesia
*Email: pirimsetiarso@unesa.ac.id

Abstract: Electrochemical analysis has carried out butylated hydroxytoluene (BHT) measurements. Cyclic voltammetry is used in this research as a qualitative-quantitative analysis of oxidation and reduction reaction processes, adsorption processes on electrode surfaces, and chemical electron transfer mechanisms. This research aims to determine the optimum deposition time and scan rate in cyclic voltammetry, the BHT standard equation, the limit of detection, and the recovery percentage. In this research, a deposition time of 25 seconds produces the highest current response of 3.89672×10^{-4} Ampere. The scan rate is 150 mV/second, producing the highest and optimum current response of 4.24561×10^{-4} Ampere. BHT standard equation $y = (4.92784 \times 10^{-6}) x + (1.25207 \times 10^{-4})$ is obtained with $R^2 = 0.99933$. The limit of detection value is 2.69683 ppm, and the recovery percentage is 101.314%. Therefore, this cyclic voltammetry method is suitable for analyzing BHT because it has high sensitivity.

INTRODUCTION

Butylated hydroxytoluene (BHT) is a chemical substance widely used as an antioxidant in packaged foods [1]. BHT is classified as a synthetic phenolic antioxidant compound [2]. BHT is incompatible with hydrochloric acid, anhydrous acid, copper steel, bases, and oxidizing agents [3]. BHT can damage the autooxidation reaction chain by donating hydrogen atoms to fat radicals, producing stable and radical-free products [4].
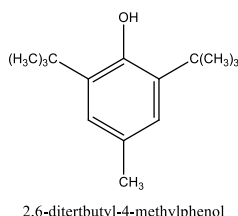

2,6-ditertbutyl-4-methylphenol

Figure 1. Butylated Hydroxytoluene Chemical Structure [5]

Adding BHT reduces free radicals so that product quality is maintained regarding texture, taste, colour, and smell. However, the use of BHT in large quantities can cause toxicity effects on the lungs and have the potential to induce tumour effects. High levels of BHT have been reported to be responsible for liver damage and are carcinogenic in animals [6]. In clinical trials, 100% BHT could cause mild irritation and sensitive skin [4]. Apart from that, applying BHT to the skin can also cause problems with dermatitis and urticaria [7].

Determination of BHT levels is often carried out using the high-performance liquid chromatography (HPLC) method. This method is popularly used in determining BHT levels because of its detection sensitivity, good separation ability, precision, and reproducibility for quantitative analysis

[8]. Sometimes, analyzing BHT levels using the HPLC method requires a long time because separating compounds in the sample depends on the type of mobile phase, flow rate, pressure, and column temperature. Besides that, an alternative method can be used to determine BHT levels in lotion, namely the voltammetry method. Voltammetry is a kind of electrochemistry method. Voltammetry methods are essential in inorganic chemistry, physical chemistry, and biology. One type of voltammetry method is cyclic voltammetry. This cyclic voltammetry method can be used as a qualitative-quantitative analysis of oxidation and reduction reaction processes, adsorption processes on electrode surfaces, and chemical electron transfer mechanisms [9]. This research is essential because it has advantages in good detection sensitivity, which can be seen from its low limit detection value [9]. This research aims to determine the optimum deposition time and scan rate in cyclic voltammetry, the BHT standard equation, the limit of detection, and the recovery percentage. Therefore, BHT content analysis was carried out using the cyclic voltammetry method.

RESEARCH METHODS

In this research, the following materials and instruments were used. There are BHT p.a. ethanol 96% for analysis, aquadest, voltammetry type 797 computrace program, working electrode, auxiliary electrode (Pt), reference electrode (Ag/AgCl), analytical balance, measuring pipette, and measuring flask.

Preparation of Main Solution

0.25 grams of BHT was weighed and dissolved in a 250 mL volumetric flask with 96% ethanol

solvent. Homogenized and stored in a dark bottle to avoid sunlight.

Preparation of BHT Standard Solution

Standard solutions are prepared by graded dilution from high to low concentration. A total of 10 mL of 1000 ppm BHT solution was pipetted into a 100 mL flask and diluted with 96% ethanol to the limit mark. Next, homogenize by shaking gently. The following is the volume obtained for BHT when dilution is carried out in stages.

Table 1. BHT standard solution calculation

BHT Concentration (ppm)	Volume (mL)
100	10 mL BHT 1000 ppm
80	80 mL BHT 100 ppm
60	75 mL BHT 80 ppm
40	66.67 mL BHT 60 ppm
20	50 mL BHT 40 ppm

The optimum Deposition Time Determination

The optimum deposition time was determined using cyclic voltammetry in 60 ppm BHT with a volume of 20 mL at a voltage of -2 to +2 V, a scan rate of 50 mV/s, and various deposition times of 5, 10, 15, 20, and 25 seconds. The highest peak deposition time determines the optimum scan rate measurement.

The optimum Scan Rate Determination

The optimum scan rate was determined using cyclic voltammetry in 60 ppm BHT with a volume of 20 mL at a voltage of -2 to +2 V, using optimum deposition time, and various scan rates of 50, 75, 100, 125, 150 mV/s seconds. The highest peak of the scan rate is used to determine the BHT standard concentration measurement to make a standard curve.

BHT Standard Equation

The standard equation is obtained from the linearity relationship between standard solutions. This research uses standard solutions for 20, 40, 60, 80, and 100 ppm BHT.

$$y = ax + b \ldots [10]$$

Information:
y = current peak
x = concentration
a = slope
b = intercept

Limit of Detection Determination

The limit of detection is the smallest concentration of BHT that the instrument can analyze.

$$LOD = \frac{3.3 \, x \, \sigma}{slope} \ldots [11]$$

Information:

Deviation standard (σ) $= \sqrt{\frac{\Sigma(xi-\mu)^2}{N}} \ldots [12]$

Slope = the value from x coefficient

Recovery Percentage Determination

The recovery percentage is one of the parameters to determine data accuracy.

$$\% \text{ recovery} = \frac{average \ measured \ concentration}{known \ concentration} \ldots [13]$$

**RESULTS AND DISCUSSION**
Optimum Deposition Time Determination

Deposition time is when the electrode is immersed in the voltammetry cell so ions depose on the electrode surface. This step aims to determine the optimum deposition time that can be used to characterize BHT in terms of the highest current response. A voltammogram indicates the BHT solution at 5, 10, 15, 20, and 25 seconds deposition times.

Table 2. Ipa and Epa of various deposition time

Deposition time (s)	Ipa (Ampere)	Epa (Volt)
5	3.56735×10^{-4}	-0.129959
10	3.73288×10^{-4}	-0.128819
15	3.80645×10^{-4}	-0.125399
20	3.83899×10^{-4}	-0.124259
25	3.89672×10^{-4}	-0.124259

Based on the voltammogram above, it is found that a deposition time of 25 seconds produces the highest current response of 3.89672×10^{-4} Ampere. The higher the deposition time applied, the higher the current read [10]. The longer the deposition time, the greater the deposition of ions on the electrode surface so that more BHT ions are deposited.

Besides that, it is known that the voltammogram shows one upward peak, which is called the oxidation peak. The BHT oxidation reaction occurs when the electrode surface is negatively charged at a negative potential, releasing+ in the phenolic group to form positively charged BHT ions accompanied by the transfer of 2 electrons [11].
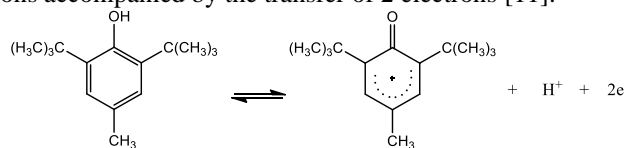
2,6-di-*tert*-butyl-4-methylphenol

Figure 3. The anodic oxidation reaction of BHT [11]

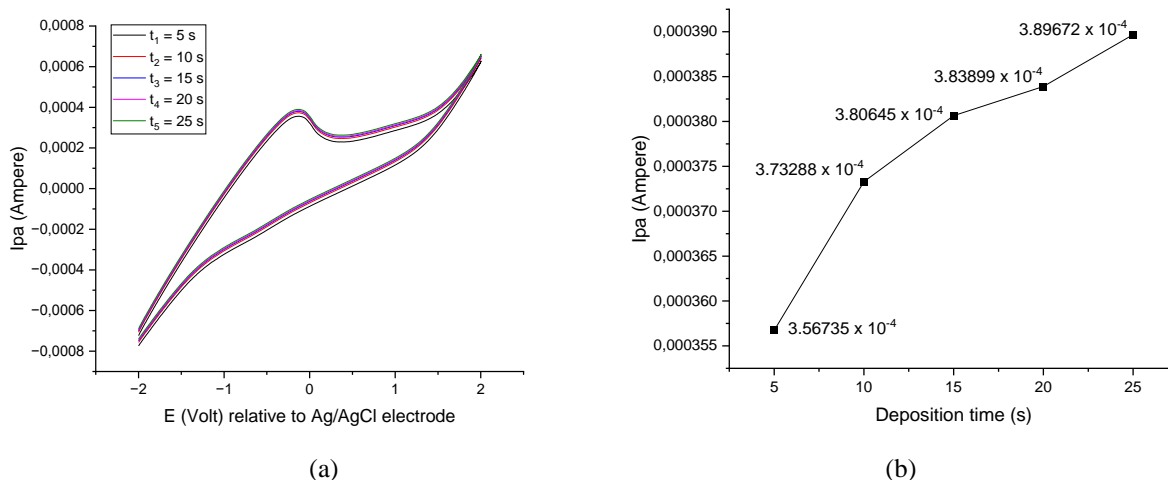|	
(a)	(b)

Figure 2. (a) Voltammogram of 60 ppm BHT at various deposition times 5, 10, 15, 20, and 25 seconds (b) curve of current vs deposition time

Optimum Scan Rate Determination

The electrode scan rate is a measure of how fast and slow the electrode scans are for analyte ions within a specific potential range. This step aims to determine the optimum scan rate that can characterize BHT regarding the highest current response. A voltammogram indicates the BHT solution at scan rates of 50, 75, 100, 125, and 150 mV/s.
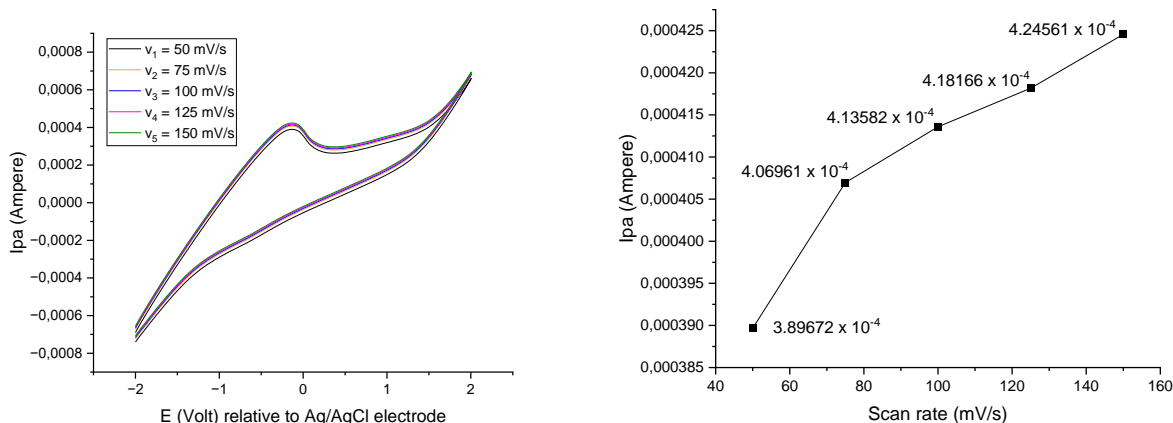

Figure 4. (a) Voltammogram of 60 ppm BHT at various scan rates 50, 75, 100, 125, and 150 mV/s (b) curve of current vs scan rate

Table 3. Ipa and Epa of various scan rates

Scan rate (mV/s)	Ipa (Ampere)	Epa (Volt)
50	3.89672×10^{-4}	-0.124259
75	4.06961×10^{-4}	-0.124259
100	4.13582×10^{-4}	-0.124259
125	4.18166×10^{-4}	-0.124259
150	4.24561×10^{-4}	-0.124259

At a 50 mV/second scan rate, the most negligible current response was 3.89672×10^{-4} Ampere with -0.124259 as potential voltage. A scan rate that is too small makes the diffusion area wider so that the diffusion rate is slower than the reaction rate. A low scan rate requires a long scanning time. As a result, the oxidation reaction of the BHT compound is almost complete, and charge transfer is not optimal. Therefore, the resulting current response is also small.

Based on the voltammogram above, the resulting current also increases as the scan rate increases. A scan rate of 150 mV/second produces the highest current response of 4.24561×10^{-4} Ampere with potential voltage (Epa) value relative at the same points, indicating that the measurement is of good precision. A high scan rate narrows the analyte diffusion layer so that the diffusion rate is faster than the reaction rate. The rapid diffusion rate causes the accumulation of analyte ions on the electrode surface [12-13]. Therefore, the resulting current response becomes higher. So, the scan rate of 150 mV/s is used as the standard solution measurement to make the BHT standard curve.

BHT Standard Equation

Standard solution measurements were carried out under optimal conditions: optimum deposition time and scan rate. Based on research that has been carried out, the optimal state of BHT in the voltammetry cell is using a deposition time of 25 seconds and a scan rate of 150 mV/second. The standard solution concentrations used in this research include 20, 40, 60, 80, and 100 ppm, so the standard equation $y = ax + b$ and the R^2 value are obtained. Below is a voltammogram of the BHT standard curve.
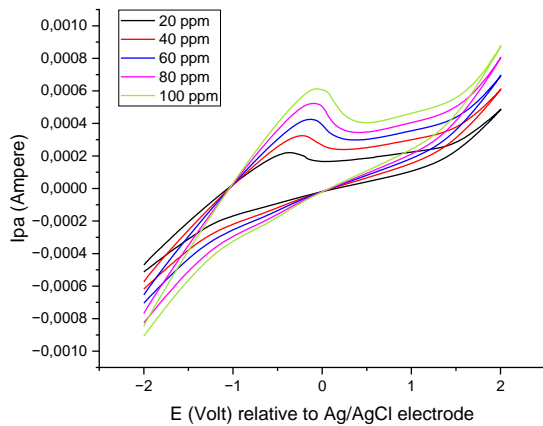

Figure 5. Voltammogram of BHT standard solution at optimum deposition time and optimum scan rate

Table 4. Ipa and Epa of BHT common solution in optimum deposition time and optimum scan rate

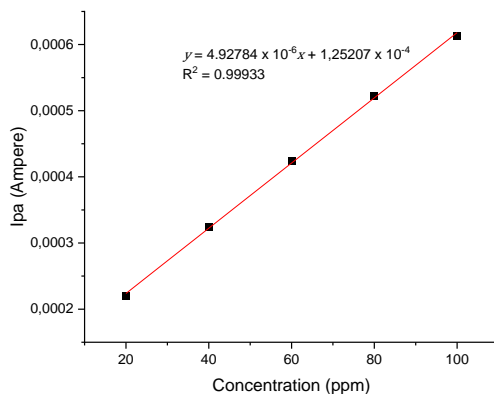| Concentration (ppm)	Ipa (Ampere)	Epa (Volt)
20	2.20006×10^{-4}	-0.372777
40	3.23713×10^{-4}	-0.227998
60	4.24561×10^{-4}	-0.124259
80	5.22920×10^{-4}	-0.092339
100	6.13186×10^{-4}	-0.066119

Figure 6. BHT Standard Curve

Based on the data above, the standard BHT equation $y = (4.92784 \times 10^{-6}) x + (1.25207 \times 10^{-4})$ is obtained with $R^2 = 0.99933$. The results of this standard equation can be used to determine the BHT concentration using the cyclic voltammetry method.

Limit of Detection Determination

The standard deviation of the residual current is required to be determined before calculating the LOD. It is known that the standard deviation of the residual current in this study is 4.02714×10^{-6} with a slope of 4.92784×10^{-6}. Therefore, it can be determined that the LOD in this measurement is 2.69683 ppm.

Recovery Percentage Determination

Recovery percentage is a value that expresses the accuracy of the data if the method is said to have good accuracy if the percent recovery range is in the field of 90 – 100% [14].

Table 6. Recovery percentage calculation

BHT concentration	60 ppm		
Repetitions	1	2	3
Ipa (Ampere)	4.24561×10^{-4}	$4,24561 \times 10^{-4}$	$4,25161 \times 10^{-4}$
Measured concentration (ppm)	60.7476	60.7476	60.8693
Average concentration (ppm)		60.7882	
Recovery percentage %		101.314	

Based on the data above, a recovery percentage above 100% indicates that the measured value for the matrix is higher than the spike value [20]. It's because of uncertainty during the calibration process, either when using or reading the instrument [21]. Also, recovery is more than 100% because the sample contains compounds that, in solution, can produce electrochemistry current that interferes with the measurement working electrode [22-23]. However, the recovery percentage of 101.314% is still said to be excellent and accurate.

CONCLUSION

A deposition time of 25 seconds produces the highest current response, 3.89672×10^{-4} Ampere. The scan rate is 150 mV/second, producing the highest and optimum current response of 4.24561×10^{-4} Ampere. BHT standard equation $y = (4.92784 \times 10^{-6}) x + (1.25207 \times 10^{-4})$ is obtained with $R^2 = 0.99933$. The limit of detection value is 2.69683 ppm, and there is a recovery percentage of 101.314%. Therefore, this cyclic voltammetry method is suitable for analyzing BHT because it has high sensitivity.

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