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ELECTROCHEMICAL TECHNIQUE FOR 1, 3-DICHLORO-2-PROPANOL ANALYSIS

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ABSTRACT: Soy sauce is widely used as a seasoning for many kinds of food. 1,3 Dichloro-2-propanol (1,3-DCP) is a toxic, semi-volatile organic liquid that is soluble in water and organic solvent. It is used in a large quantity as an intermediate in epichlorohydrin production. 1,3-DCP is a major raw material in the chemical paper industry, but it is a problem in the production of foods, such as soy sauces and other acid-hydrolyzed vegetable proteins. The normal method to analyze 1,3-DCP is an expensive and time-consuming GC-MS technique using a highly purified sample. Our purpose was to reduce the expense and time of the analysis. Therefore, this research focused on improvement of 1,3-DCP analysis methodology by using an electrochemical technique. We produced a carbon paste electrode, which was used as the working electrode. We studied the suitable conditions for analysis by using a voltammetry technique; electric potential and NaOH in oxidation reaction of 1,3-DCP and an amperometry technique; interval time of reaction at electrode surface (5 and 10 minutes), stirring rate (100, 300 and 500 rpm). It was found that the electric potential and the interval time of oxidation reaction for 1,3-DCP analysis were 1.3 V. and 5 minute intervals, respectively. Moreover, we found that 4.0 M NaOH and 100 rpm stirring rate were suitable for this analysis. The result of our research were 0.02 mg/dm^3 detection limit, 81.27 % recovery, 13.339 ppm sensitivity, 0.67-4.67 ppm linear range, 6.95 % RSD of solution preparation, 3.95 % RSD of injection and 5.15 % RSD of the carbon paste working electrode.

Keywords: 1,3 Dichloro-2-propanol, Soy sauces, Electrochemical technique, Halohydrin, Ephichlorohydrin,

1. INTRODUCTION

Seasoning sauce is produced from acid hydrolyzed vegetable protein [1] that is defatted using hydrochloric acid at high temperature. The production process results in chloropropanol compounds, for example 3-monocholropropane 1,2-diol (3-MCPD) and 1,3-Di-chloropropanol (1,3-DCP), that are toxic and carcinogen [6]. 1,3-DCP is formed from reaction of 3-MCPD and has been found in soy sauce and other seasoning sauce. When both 3-MCPD and 1,3-DCP are found in sauce, the amount of 3-MCPD is always higher than 1,3-DCP by a ratio of 20:1. Therefore, if we can determine the 1,3-DCP concentration in sauce, we can determine the 3-MCPD concentration too. Although 1,3-DCP is usually analyzed by an expensive and time-consuming GC-MS technique using a highly purified sample [4], the purpose of this research was to reduce the analysis expense and time. Therefore, we focused on developing an electrochemical technique to analyze 1,3-DCP. This required producing a carbon paste electrode to use as the working electrode for examining the reaction capacity.

2. EXPERIMENT

2.1 Reagent and Materials

1,3-Dichloropropanol (1,3-DCP) 98 % and other reagent were purchased from Aldrich. All the solutions were prepared with analytical grade reagents and Milli-Q water.

2.2 Electrode preparation

The working electrode was prepared by thoroughly hand-mixing 5 g graphite powder and 1mL of silicone oil in a mortar with pestle. This paste was placed in a cavity on electrode body (glass tube ϕ 5 mm) in contact with a copper wire and smoothed on clean paper until it had a shiny appearance.

2.3 Apparatus

All voltammetric measurements were performed using a VA Stand 663 Voltametric analyzer (Metrohm,Herisau,Switzerland) and a Potentiostat (Autolab model PGSTAT 20). The three electrode assembly cell consisted of the following : carbon paste electrode as working electrode, Ag/AgCl in 3 mole/L KCl as a reference electrode and platinum wire as an auxiliary electrode.

2.4 Procedure

2.4.1 Cyclic voltammetry of 1,3-DCP

Suitable electric potential in the reduction-oxidation (redox) reaction and effect and concentration of sodium hydroxide to oxidation current.

2.4.2 Amperometric Determination of 1,3-DCP

Effect of reaction time and rotation rate in 1,3-DCP analysis.

2.4.3 Analytical parameters for 1,3-DCP determinations

Detection limit, % recovery, sensitivity, linear range, % RSD of injection and % RSD of the working electrode.

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry of 1,3-DCP

3.1.1 The suitable potential in oxidation-reduction

As shown in Fig. 1 below, the cyclic voltammogram of 2,000 ppm of 1,3-DCP did not show an oxidation and reduction peak. Therefore, we tried to activate the redox reaction of 1.3-DCP using NaOH.

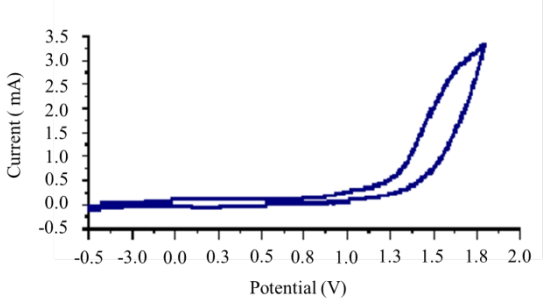
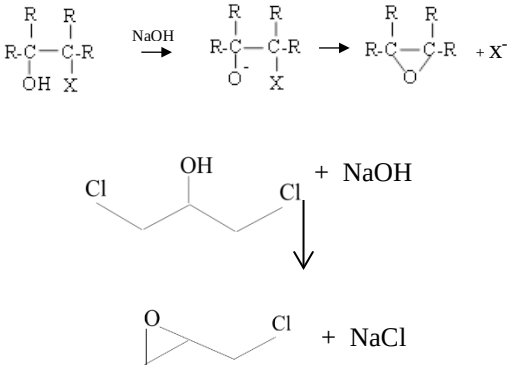


Fig. 1 Cyclic voltammogram of 2,000 ppm 1,3-DCP in water using carbon paste electrode with scan range from -0.5 to 2.0 V and scan rate of 1 V/sec.

A halohydrin reacts with sodium hydroxide solution to produce an epoxide [9]. 1,3-DCP is a halohydrin compound, so it can react with sodium hydroxide to produce epichlorohydrin, sodium chloride and water. This reaction is shown in the following equation [10].



Reaction of halohydrin and NaOH

3.1.2 The effect and concentration of sodium hydroxide to oxidation current

As shown in Fig. 2 below, the cyclic voltammogram of 2,000 ppm 1,3-DCP in 0.1 M NaOH solution showed an anodic current peak at about 1.45 V [3].

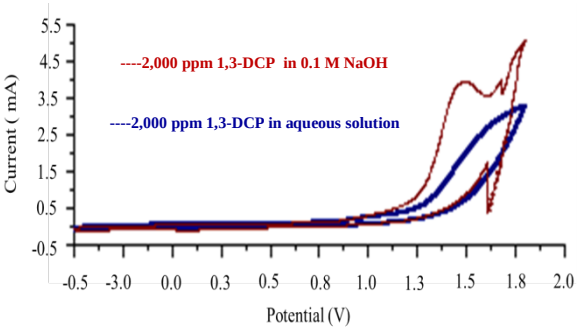


Fig.2 Cyclic voltammogram of 2,000 ppm 1,3-DCP on carbon paste electrode with condition : scan range from -0.5 to 2.0 V,Scan rate of 1 V/sec, with NaOH (red line) and without NaOH (Blue line).

As shown in Fig. 3(a) cyclic voltammograms of 2,000 ppm.1,3-DCP in various concentrations of NaOH, the oxidation peaks occurred in the range of 1.3-1.5 V.

Figure 3(b) showed that the peak anodic current increased as NaOH concentration was increased from 0.1 to 4.0 M, but decreased at 8.0 M. Therefore, a sodium hydroxide concentration of 4.0 M produced the highest peak anodic current. Electric potential was fixed at 1.3 V throughout this amperometric experiment.

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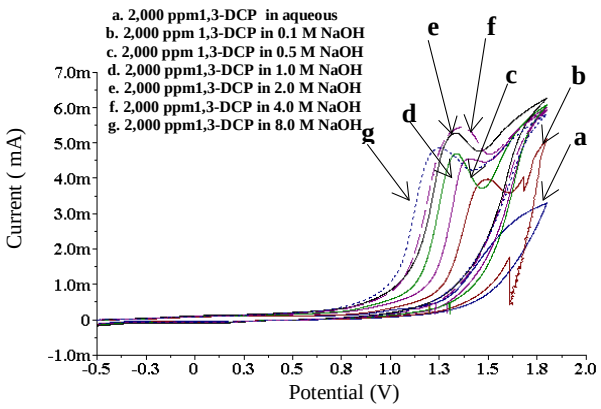
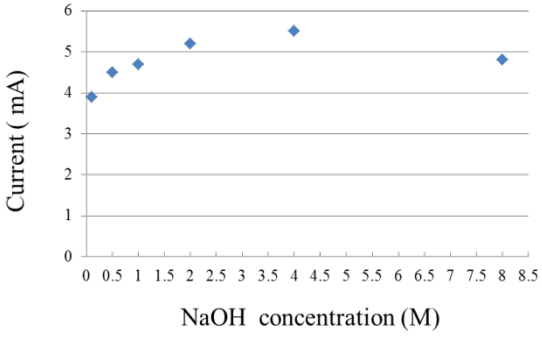


(a.)

Fig.3 (a) The cyclic voltammograms of 2,000 ppm 1,3-DCP in different concentrations of NaOH using carbon paste electrode with scan range from -0.5 to 2.0 V and scan rate of 1 V/sec.



(b)

Fig. 3(b) The peak anodic current at NaOH concentrations from 0.1 to 8.0 M

3.2 Amperometric Determination of 1,3-DCP

Figures 4(a and b) showed the amperometric response obtained by continuous addition of 10 µL 20,000 ppm of 1,3-DCP in 4.0 M NaOH at 5 and 10 minute intervals, respectively. We found that the sensitivity of the two intervals was nearly equivalent, but that R^2 of the 5 minute interval was higher than R^2 of the 10 minute interval as shown in Fig 4(c). Therefore, we selected the 5 interval for the next experiment in which rotation speed was varied**.**

Figures 5(a, b, and c) showed the amperometric response obtained by continuous addition of 20,000 ppm 1,3-DCP at 5 minute intervals using 100, 200 and 300 rpm rotation speeds. We found that a rotation speed of 100 rpm gave the highest sensitivity as shown in Fig. 5(d).

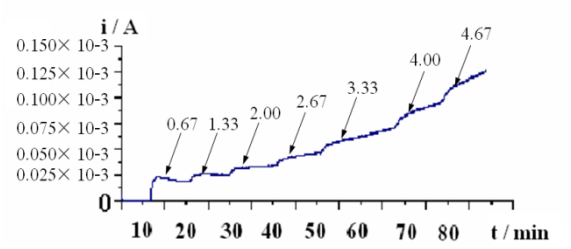


Fig.4(a) 5 min interval

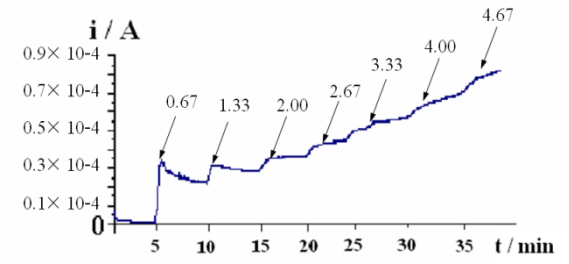


Fig.4(b) 10 min interval

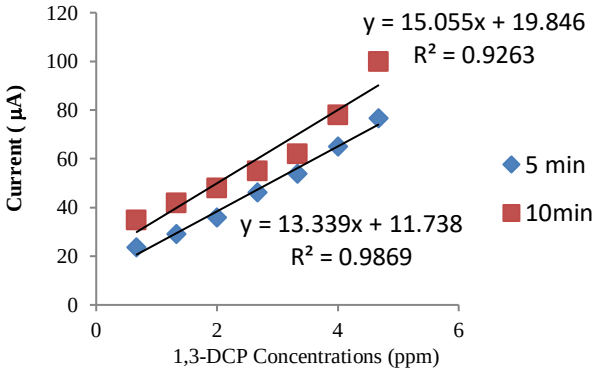
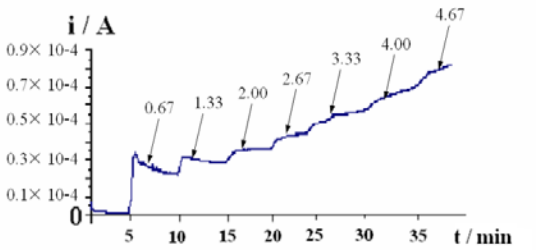


Fig.4(c)

Fig.4(a,b,c) Amperometric response and analytical curve for addition of 2000 ppm 1,3-DCP at 5 and 10 minute intervals. Experimental conditions: E = 1.3 V, rotation speed 100 rpm



Fig,5(a) rotation speed 100 rpm

3.3 Analytical parameters for 1,3-DCP determinations

Optimal conditions of this experiment were addition of 1,3-DCP into 4 M NaOH at 5 minute intervals with 1.3 V applied electric potential and 100 rpm rotation speed. These

conditions resulted in 0.02 ppm detection limit, 81.27% recovery, 13.339 ppm sensitivity, 0.67-4.67 ppm linear range, 6.95% RSD of solution preparation, 3.95% RSD of injection, and 5.15% RSD of the carbon paste working electrode.

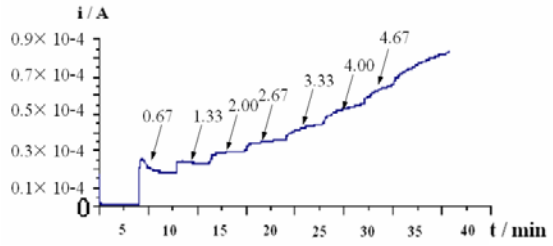
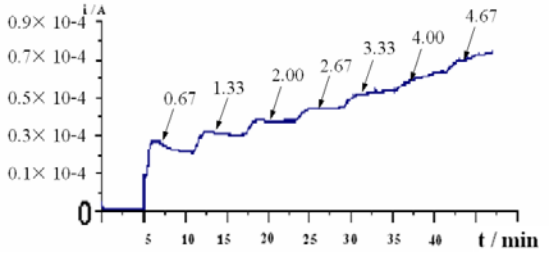


Fig.5(b) rotation speed 200 rpm



Fug.5(c) rotation speed 300 rpm

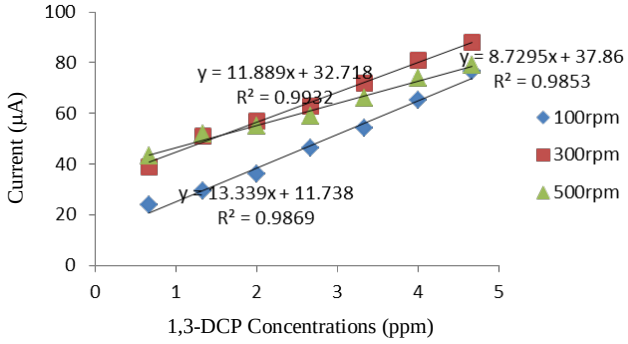


Fig.5(d)

Fig.5(a, b, c, d) Amperometric response of continuous addition 1,3-DCP 20,000 ppm at 5 minutes interval, E=1.3 V using 100 200 and 300 rpm rotation speeds.

The detection limit (LOD) of 0.02 ppm for 1, 3-DCP using this experimental method can be used to analyze for 1,3-DCP because the maximum contamination amount of 1,3-DCP allowed in Thailand is 1 ppm. The concentration of 3-MCPD is always 20 times greater than 1,3-DCP. and 3-MCPD. Therefore, we deduced that our experimental method can be used to analyze 1,3-DCP and 3-MCPD in other samples. However, the detection of 1,3-DCP by GC-MS Headspace is the ppb level [7] So, we expect to improve results by using other materials, such as glassy carbon, as the working electrode.

4. CONCLUSION

This research showed that 1,3-DCP can be analyzed using an electrochemical technique to detect the anodic current produced from the reaction of a halohydrin with NaOH solution. Detailed observation was found that the electric potential and the interval time of oxidation reaction for 1,3-DCP analysis were 1.3 V. and 5 minute intervals, respectively. The suitable stirring rate were 4.0 M NaOH and 100 rpm. Finally, the research presented here showed the 0.02 mg/dm^3 detection limit, 81.27 % recovery, 13.339 ppm sensitivity, 0.67-4.67 ppm linear range, 6.95 % RSD of solution preparation, 3.95 % RSD of injection and 5.15 % RSD of the carbon paste working electrode.

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