

**Modification of Screen Printed Carbon Electrode (SPCE) with Fe<sub>3</sub>O<sub>4</sub> for the Determination of Nitrite (NO<sub>2</sub><sup>-</sup>) in Squarewave Voltammetry****Erica Marista Rosida, Ani Mulyasuryani\*, Rachmat Triandi T**Chemistry Department, Faculty of Mathematics and Natural Sciences,  
Brawijaya University, Malang, Indonesia

\*email: mulyasuryani@ub.ac.id

**Received** April 12, 2017; **Accepted** September 01, 2017; **Available online** November 30, 2017**ABSTRACT**

Nitrite is one of the food preservatives that the government permits, but on the use of over limits can cause endanger health, so it is necessary to control the content of nitrite in the food. Modification of electrodes on a screen printed carbon electrode (SPCE) with Fe<sub>3</sub>O<sub>4</sub> has been successfully done for determination of nitrite. Modification of the electrode has been done by electrodeposition with cyclic voltammetry. Electrodeposition successfully performed with an electrolyte solution of FeCl<sub>3</sub> in ethanol. Selection of the optimum drying temperature modified electrode obtained based on the respond of the solution of nitrite in Britton Robinson buffer pH 8. The result of the modification electrode used for the determination of nitrite with squarewave voltammetry method. Reaction between Fe<sup>3+</sup> with nitrite a basis for determining nitric indirectly measured so that the peak current is the peak current of Fe<sup>3+</sup> of about 0,55 V vs Ag/AgCl. The results showed nitrite measurements with this method has a detection limit of 1.3 x 10<sup>-8</sup> M.

**Keyword:** Nitrite, Squarewave Voltammetry, Electrodeposition, Fe<sub>3</sub>O<sub>4</sub>**INTRODUCTION**

Nitrite is one of the food preservatives that the government permits, but on the use of over limits can cause endanger health. The maximum limit to use of nitrite as a food preservative for meat is 30 mg/ kg, for cheese is 20 mg/ kg. Nitrite can bind with the amino and amide contained in the protein in meat to form derivative nitrosamines toxic which is suspected to cause cancer (Sinaga, Naibaho, & Situmorang, 2013). Thus, it is necessary to control the nitrite content in food. Nitrite is an electroactive compound which can be reduced and oxidized so it can be analyzed by an electrochemical method.

The electrochemical method has attracted attention because this method provides a cheap and quick analysis that has been developed to get a sensitive and selective method (Renedo, Alonso-Lomillo, & Martínez, 2007). One way to improve the selectivity and sensitivity is the modification of electrode (Yildiz, Oztekin, Orbay, & Senkal, 2014). Screen-printed electrodes (SPE) is a good electrode device reference electrode, the electrode support and the working electrode is printed on the same substrate surface (Hayat & Marty, 2014). Modification of surface electrode can be done by adding various substances such as metal oxides (Li et al.,

2014), a polymer (Lin, Vasantha, & Ho, 2009) and enzymes (Soukup & Vyt<sup>ˇ</sup>, 2010).

Determination of nitrite in the voltammetry method has been studied in a variety of modifications to the working electrode. In 2014 the working electrode modified with Fe<sub>2</sub>O<sub>3</sub>/GO, Pt as a supporting electrode and Ag/AgCl as the reference electrode was used for the determination of nitrite in phosphate buffer with differential pulse voltammetry method (Radhakrishnan, Krishnamoorthy, Sekar, Wilson, & Kim, 2014). In 2015, the working electrode modified with poly (diallyldimethylammonium)-Fe<sub>3</sub>O<sub>4</sub> that is immobilized on multiwalled carbon nanotubes (MWCNT) (Qu, Dong, Wang, & Xing, 2015). The result of these modifications was used for the determination of nitrites in cyclic voltammetry. In 2015, the surface of electrode was modified with a mixture of myoglobin that immobilized on a single walled nanotubes carbon nafion then superimposed with the film on the surface of the graphite electrode (Turdean & Szabo, 2015).

The modified electrode used for the determination of nitrite in meat product samples by square wave voltammetry method. In 2008, the determination of nitrite directly and indirectly to do with the method of the DPP (Differential pulse polarography) (Yilmaz & Somer, 2008). Determination of nitrite was directly known from current peaks that appear

at potential -1.4 V. As for the determination of nitrite indirectly with the addition of sulphite solution. Sulfate has a reduction potential of +0.172 V vs SHE and the potential reduction of nitrite to NO at +1 V vs SHE. Based on the value of the standard potential that sulfite can reduce nitrite to NO and sulfite itself oxidised to sulphates. Sulfites are electroactive and has a peak greater than nitrite, on the basis that nitrites can be analyzed indirectly.

In this study, a modification of electrode carried on the screen printed carbon electrode (SPCE) with Fe<sub>3</sub>O<sub>4</sub> for the determination of nitrite. Modifications electrode with Fe<sub>3</sub>O<sub>4</sub> has been applied to a chemical sensor because it has a high conductivity is 10<sup>2</sup>-10<sup>3</sup> Ω<sup>-1</sup>cm<sup>-1</sup> (Blaney & Blaney, 2007), may increase the electron transfer (Jin-lei et al., 2011), can increase selectivity, sensitivity as well as having good stability (Zhang, Kang, Xue, & Sun, 2013).

Synthesis of Fe<sub>3</sub>O<sub>4</sub> conducted by electrodeposition directly on the working electrode SPCE with cyclic voltammetry method. Electrodeposition by cyclic voltammetry is preferred because can show reaction phenomenon based on voltammogram. The determination of nitrite is done with squarewave voltammetry method, because the method has a low detection limits and speed of scanning up to 1 V / s. Response mechanism that occurs on the electrode surface modification of Fe<sub>3</sub>O<sub>4</sub> is nitrite oxidized to nitrate by Fe<sup>3+</sup> and Fe<sup>3+</sup> itself is reduced to Fe<sup>2+</sup>. Nitrite to nitrate oxidation potential of -0.01 V vs SHE in an alkaline medium and the potential reduction of Fe<sup>3+</sup> was 0.77 V vs SHE. Thus the reaction of Fe<sup>3+</sup> with nitrite can last and the current response is a peak current voltammetry reduction of Fe<sup>3+</sup> and the measurement of nitrite in the study done indirectly.

## EXPERIMENTAL SECTION

### Materials

The materials used iron(III) chloride hexahydrate from Merck with analytical grade, ethanol from Merck was used analytical grade, sodium nitrite from Merck with analytical grade, boric acid for analysis from Merck, sodium hydrogen phosphate from Merck, sodium dihydrogen phosphate from Merck, sodium hydroxide from Merck with analytical grade, phosphoric acid 85%, acetic acid 99% and distilled water.

### Instruments

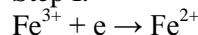
The instruments used analytical balance (Mettler Toledo AL204), pH meter (Trans Instrument Sensz pH), magnetic stirrer and stirrer (IKAMAG®RH), oven (Mettmert), micro pipette (Accumax pro), screen printed carbon electrode (SPCE) BI 1302 (Quasense Inc.), potentiostat / Galvanostat Uniscan PG581, FEI Inspect S50 SEM and EDAX AMETEK.

### Procedures

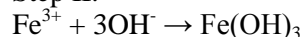
#### Modification of SPCE

Fe<sub>3</sub>O<sub>4</sub> electrodeposition process developed from methods that have been made (Marques et al., 2008). In this study, electrodeposition performed with cyclic voltammetry method. electrolyte solution FeCl<sub>3</sub> 0.05M made with ethanol. Electrodeposition performed by scanning twice. First, the scanning is done on the potential range -0.5 - 1 V, the scan rate of 100 mV/s with the number of cycles are 20 cycles. Second, the scanning is done after the addition of 0.01 M NaOH as 2.5 μL just above the working electrode in the potential range -0.5 - 1 V, the scan rate of 100 mV/s with the number of cycles are 10 cycles. Results electrodeposition and then dried in an oven. The reaction equations that may occur in the electrodeposition process:

Step I:



Step II:



#### Optimization of Drying Temperature

Optimization is done on the drying temperature SPCE electrodeposition modified with ethanol. Results electrodeposition then dried in an oven at drying temperature is 35, 40, 45, 50 and 55 °C.

#### Determination of Nitrite

SPCE modified Fe<sub>3</sub>O<sub>4</sub> by electrodeposition with optimum drying temperature used for the measurement of nitrite in different supporting electrolyte solution that is Britton Robinson buffer and phosphate buffer at pH 8. The measurements carried out with squarewave voltammetry method with the potential range -1 to 1 V, the high pulse is 0.5 V and a frequency is 5 Hz. The measurement of nitrite carried out on a range concentrations of nitrite 10<sup>-6</sup> – 10<sup>-7</sup> M.

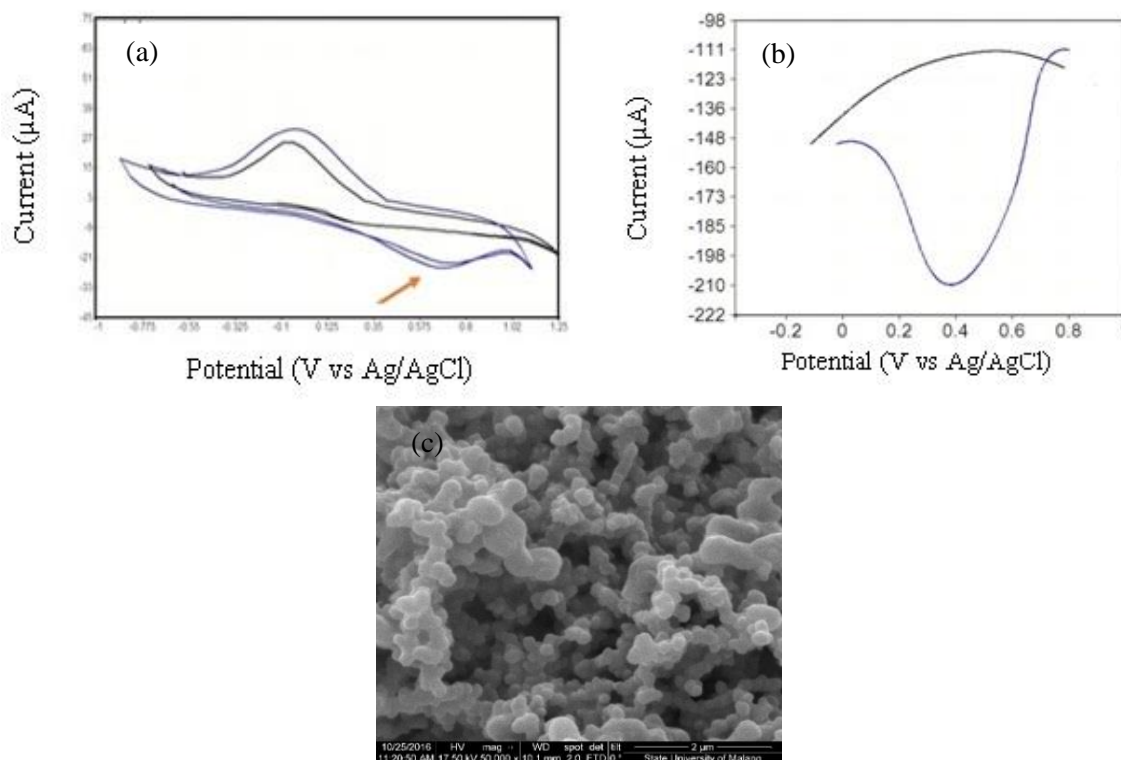
## RESULTS AND DISCUSSION

### Characterization of Modified Electrodes

The test results of the electrode modification carried by cyclic voltammetry in Britton Robinson buffer solution pH 8 and 1 mM nitrite in Britton Robinson buffer pH 8 at a potential range -1 to 1 V, the scan rate 0.1 V/s. The test results of the modified electrode shown in **Figure 1(a)** and **Table 1**. Analysis nitrite was also carried with squarewave voltammetry shown in **Figure 1(b)**. The success of the modified electrode is known of the nature of the electroactive shown E<sub>pk</sub> value of Fe<sup>3+</sup>.

**Figure 1(a)**, the test results on the electrode modified by cyclic voltammetry method in Britton Robinson buffer solution and 1 mM nitrite in Britton Robinson buffer. The results of the test with Britton Robinson

buffer solution showed a peak potential of oxidation at -0.034 V vs Ag/AgCl. The composition of Britton Robinson buffer is boric acid, phosphoric acid and acetic acid. Borate can form complexes with Fe (III). Borate has a standard reduction potential of -1.1 V vs SHE and Fe (III) has a standard reduction potential of 0.77 V vs SHE. Based on the potential standard value, Fe (III) can oxidize tetrahydroxyborate be boric acid so that the oxidation peak appearing a peak potential of oxidation borate. Tetrahydroxyborate oxidation potential was 0.11 V vs Ag/AgCl, while the research is -0.034 V vs Ag/AgCl. Differences in both the oxidation potential peak due to different measurement conditions.

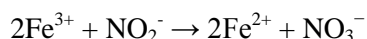


**Figure 1.** Voltammograms at an electrode modified with a) cyclic voltammetry in BR buffer solution (black) and 1 mM solution of nitrite in BR buffer (blue). b) voltammogram squarewave voltammetry in BR buffer solution (black) and 0.1 ppm nitrite in Britton Robinson buffer (blue). c) SEM Results

**Table 1.** The peak current generated at the electrode modified Fe<sub>3</sub>O<sub>4</sub> by cyclic voltammetry

SPCE Electrode	NaNO <sub>2</sub> test				Buffer test			
	E <sub>pk</sub> (V)	I <sub>pk</sub> (µA)	E <sub>pa</sub> (V)	I <sub>pa</sub> (µA)	E <sub>pk</sub> (V)	I <sub>pk</sub> (µA)	E <sub>pa</sub> (V)	I <sub>pa</sub> (µA)
Modified Fe <sub>3</sub> O <sub>4</sub>	0.68	-15.9	0.034	-23.5	-	-	-0.045	19.6

Voltammogram of nitrite solution 1 mM Britton Robinson buffer media showed a peak current of Fe<sup>3+</sup> at a potential of 0.68 V vs Ag/AgCl. This indicates an electroactive material that can oxidize nitrite is Fe<sub>3</sub>O<sub>4</sub>. This is supported by the results of SEM with spherical morphology showing the morphology of Fe<sub>3</sub>O<sub>4</sub> as in **Figure 1(c)**. In this case Fe<sub>3</sub>O<sub>4</sub> as a modifier which can oxidize nitrite to nitrate by Fe<sup>3+</sup> as in the following equation:



Response mechanism that occurs on the electrode surface modification of Fe<sub>3</sub>O<sub>4</sub> is nitrite oxidized to nitrate by Fe<sup>3+</sup> and Fe<sup>3+</sup> itself is reduced to Fe<sup>2+</sup>. Potential oxidation of nitrite to nitrate standard of -0.01 V vs SHE in an alkaline medium, and a standard potential reduction of Fe<sup>3+</sup> was 0.77 V vs SHE. Thus the reaction of Fe<sup>3+</sup> with nitrites can be spontaneous. Ion Fe<sup>3+</sup> excess of the reaction was reduced to Fe(II). It is the basis for the determination of nitrite in the Fe<sub>3</sub>O<sub>4</sub> indirectly.

**Figure 1(b)** is a voltammogram from squarewave voltammetry method of Britton Robinson buffer solution and 0.1 ppm nitrite in Britton Robinson buffer on the electrode modified. In this result, the voltammogram Britton Robinson buffer solution does not show the flow from the reduction of Fe<sup>3+</sup> this is due to Fe<sup>3+</sup> oxidize tetrahydroxyborate borates, which is one composition of Britton Robinson buffer. But voltammogram result from a solution of 0.1 ppm nitrite in Britton Robinson buffer appears the peak reduction of Fe<sup>3+</sup> in this case the Fe<sup>3+</sup> acts as an oxidant for nitrite. Potential oxidation of nitrite to nitrate occurred at -0.01 V vs SHE, whereas the oxidation potential tetrahydroxyborate boric occur in the oxidation potential of 1.1 V vs SHE. Thus, based on the oxidation potential of both, the Fe<sup>3+</sup> will be easily oxidizes nitrite to nitrate. Thus SPCE electrode modified with Fe<sub>3</sub>O<sub>4</sub> can be used for the measurement of nitrite indirectly with squarewave voltammetry method.

#### Selection of Optimum Drying Temperature

According to the **Table 2** can be seen that of the five drying temperatures, the peak current at temperatures above 40 °C did not show a significant increase or decrease. This suggests that the drying of the electrode modified to eliminate the remnants of the solvent can be achieved with a minimum

temperature of 40 °C for 30 minutes. The drying temperatures of modified electrode also affect to potential electrode value. It is because temperature have affects to the formation of Fe<sub>3</sub>O<sub>4</sub>. Based on the Nernst equation, the potential linked to the concentration of Fe<sup>3+</sup> to Fe<sup>2+</sup>:

$$E = E^0 + \frac{2,303 RT}{nF} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

Potential reduction of Fe (III) of this research is 607 - 637 mV vs Ag/AgCl. This shows the potential value of shifting toward more positive than E<sup>0</sup> is 0.55 V vs Ag/AgCl. This indicates that the concentration of Fe<sup>3+</sup> greater than the concentration of Fe<sup>2+</sup> of Fe<sub>3</sub>O<sub>4</sub> on the electrode. It can be seen from the results of SEM of **Figure 1(c)** which generates the percentage ratio of Fe and O is 1: 2 that are likely to form FeOOH. In an electrochemical process, FeOOH is an intermediate product for the synthesis of Fe<sub>3</sub>O<sub>4</sub> (Fajaroh, Setyawan, Widiyastuti, & Winardi, 2012). It needs to do further analysis to prove the result of the synthesis is formed.

Based on **Table 2**, the peak potential shifts resulting from the fifth drying temperature. At the drying temperature 35-50 °C at intervals of 5 °C, a potential shift slightly toward more negative.

**Table 2.** Influence of drying temperature electrode modified to test 1 mM solution nitrite in Britton Robinson buffer pH 8

Variable	Average	
Temperature	E <sub>pk</sub> (mV)	I <sub>pk</sub> (μA)
35	637	3,53
40	615	7,42
45	627	7,31
50	607	7,75
55	631	3,64

This indicates that the concentration of Fe<sup>3+</sup> decreases, so that the reduction potential of Fe<sup>3+</sup> is shifting toward more negative. However, at a higher temperature at a temperature of 55 °C reduction potential of Fe<sup>3+</sup> to be more positive, it indicates that higher temperatures will result in a concentration of Fe<sup>3+</sup> are getting bigger because of the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>. Selection of the optimum drying temperature is based on I<sub>pk</sub> great value with standard E<sub>pk</sub> approaching standart potential reduction of



Fe<sup>3+</sup>. So that to determine of nitrite used the drying temperature of 50 °C because potential peak is generated peak of 0.55 V vs Ag/AgCl with a higher peak currents.

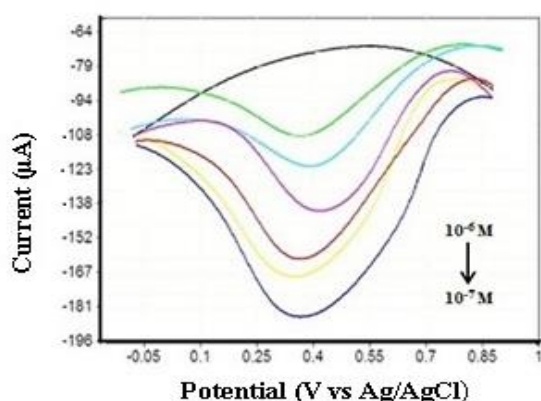
### Determination of Nitrite

#### Effect of Supporting Electrolytes for Nitrite

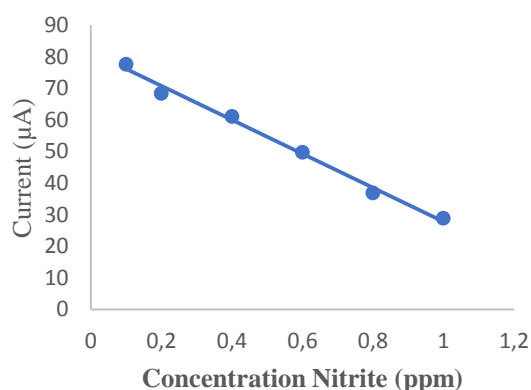
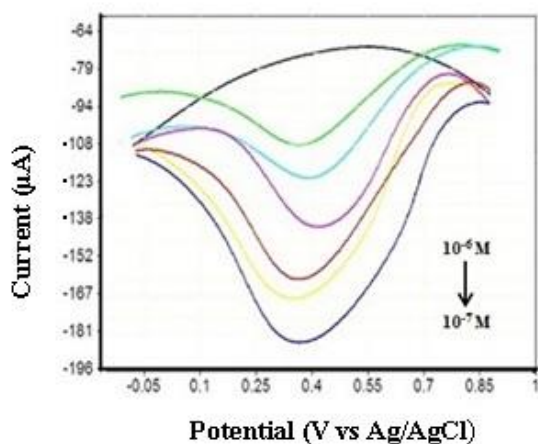
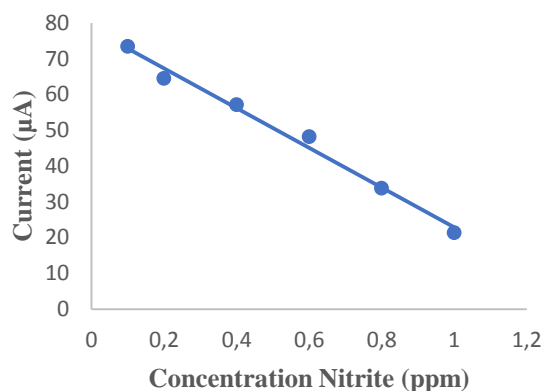
Determination of nitrite is done with methods squarewave voltammetry in a potential range of -1 to 1 V, a high pulse 0.5 V and frequency of 5 Hz. Measurement nitrite is done in two different supporting electrolyte solution is Britton Robinson buffer 0.04 M pH 8 and 0.1 M phosphate buffer pH 8. Measuring nitrite performed at concentrations of 0; 0.1; 0.2; 0.4; 0.6; 0.8; 1 ppm, the result measurements shown in **Figure 2** and **Figure 3**.

From the measurement results nitrite in Britton Robinson buffer in figure 2 the linear regression equation  $I_p = -55.442 [NO_2] + 78.34$ . The gradient of the equation shows the measurement sensitivity is 55.45 uA/ppm and

accuracy of measurements obtained from R<sup>2</sup> regression equation is 0.989. The limit detection of this measurement is 0.013 ppm. While voltammogram measurement results nitrite in phosphate buffer is shown in figure 3. From the measurement results obtained by the linear regression equation  $I_p = -53.616 [NO_2] + 79.718$ . The gradient of the equation shows the measurement sensitivity is 53.616 uA/ppm and accuracy of measurements obtained from the regression equation R<sup>2</sup> is 0.9927. The limit detection of this measurement is 0.013 ppm. Based on the results of the two measurements, both have the same limit detection, but give different sensitivities. Measurement of nitrite in Britton Robinson buffer medium has a higher sensitivity than to phosphate buffer. This is because the composition of Britton Robinson buffer is phosphate acid, boric acid, acetic acid and sodium hydroxide so that it has a greater conductivity than the phosphate buffer.



**Figure 2.** Voltammogram measurements of nitrite in Britton Robinson buffer and curve concentration vs high peak currents of nitrite in Britton Robinson buffer.



**Figure 3.** Voltammogram measurement nitrite in phosphate buffer and curve concentration vs high peak currents of nitrite in phosphate buffer.

## CONCLUSION

Modification electrode of screen printed carbon electrodes (SPCE) with Fe<sub>3</sub>O<sub>4</sub> can be electrodeposition with ethanol solvent. Drying temperature of electrode can affects the formation of Fe<sub>3</sub>O<sub>4</sub> and the optimum drying temperature occurred at 50 °C. The result of modification electrode can be used for the determination of nitrite with squarewave voltammetry method. The measurement results of nitrite in britton robinson buffer and phosphate buffer medium have the same limit detection is 0.013 ppm.

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