Electroanalysis of Formaldehyde Using Electrodeposited Nickel on Glassy Carbon Electrode

Akbar Syaifariz, Cepi Kurniawan

Universitas Negeri Semarang, Indonesia

Abstrak

Formaldehyde in many cases was found in foods as a preservative or as a result of polymer degradation from food containers. As matter of fact, formaldehyde is carcinogenic, irritant, and toxic to the body, so an efficient analytical method is needed to detect formaldehyde. The analytical method using electroanalysis is used because it can be fast, accurate, inexpensive, and easy to operate. Electroanalysis of formaldehyde using nickel electrodes deposited on *Glassy Carbon* (GC) has been carried out using cyclic voltammetry technique. The variation of nickel deposition time for 300 seconds (GC-Ni5m) and 600 seconds (GC-Ni10m) was carried out to determine its effect on formaldehyde detection ability through analysis of electroanalytical activity and the resulting detection and quantification limits. Through the cyclic voltammetry technique, two types of linear ranges were used; low concentrations (0.1–50 ppm) and high concentrations (50–500 ppm). The detection limits for GC-Ni5m were 33.1 ppm (low concentration) and 49.7 ppm (high concentration), while GC-Ni10m were 35.8 ppm (low concentration) and 69.9 ppm (high concentration). The electroanalytical method was compared with the spectrophotometric method using Schiff's reagent with a detection limit were 17.8 ppm (low concentration) and 106.6 ppm (high concentration).

Kata kunci : Electroanalysis, Formaldehyde, Nickel electrode, Glassy Carbon, Schiff's Reagent.

Introduction

Formaldehyde was found in several foods in Indonesia as a preservative agent. Indonesian food and drugs agency (BPOM) found, there were eight brands of noodles and tofu in Jakarta and salted fish in Makassar contains formaldehyde. Moreover, in Java, Sulawesi, and Lampung as much as 56% of foods from 700 samples were known to contain formaldehyde (Singgih, 2017). Besides addictive agent factors, formaldehyde is also found in several drinks and water because of degradation of its container, like *Polyethylene Tereftalat* (PET) (Itnawita *et al*., 2014), *High-density polyethylene* (HDPE) (Barrang *et al*., 2018), because of that, people consume until 0,2 mg/person each day just from drinking water (Feron *et al*., 1991). On the other hand, formaldehyde has reactive nature and strongest electrophilic if compare with other aldehyde compounds (El Sayed *et al*., 2016), its nature can cause several effects to the body like allergic, neurotoxicity, respiratory disorders, and carcinogen (Tang *et al*., 2009).

Because of its Harmful effect on the body, researchers need to determine formaldehyde effectively. The laboratory Analytical methods for determining formaldehyde, usually use supporting instruments like UV-Vis, Gas chromatography, or high-performance liquid chromatography which need time consumption and cost for analytics. Because of that, nowadays many researchers develop analytical formaldehyde methods to find quick and costless methods. Currently, electrochemistry is widely used for determination analytes methods, because it has some advantage properties like accurate, quick and costless, and easy to use for quantitative analytical methods (Ehsan & Rehman, 2020; He *et al*., 2013).

Nickel have known can be used for formaldehyde oxidation catalytic, Trivedi *et al.* (2018), was used nickel deposited on glassy carbon electrodes for the determination of formaldehyde with good results. But, only deposited for 60 seconds which was determined in formaldehyde. Novitasari *et al.* (2015) said, when the time during deposition was short, it will form the thin layer with heterogeneous surface morphology and it has less durable when compared with a long duration. This research will focus on the electroanalytic of formaldehyde using electrodeposited nickel on Glassy Carbon electrodes with variation in deposition time at 300 and 600 seconds through comparing on electroanalytical activity and its effect on detection limit.

Methods

Reagents and Equipment

Schiff's reagent (Pararosaniline HCL with sulfite) was reagent grade from Merck for UV-Vis methods, $NiSO_4.6H_2O$, KOH, H_2SO_4 97%, Formaldehyde 37%, $NaBH_4$ was purchased from Merck, water double distilled (Aquabidest), water distilled (aquadest), Screen-printed carbon electrode (SPCE) was purchase from ZeamerPeacock, Glassy Carbon electrode (ø 3 mm) as working electrode, platinum wire as counter electrode and Ag/AgCl as a reference electrode. The characterization was used Potentiostat (Rodeostat), ATR-FTIR, SEM, and UV-Vis.

Electrodeposition methods

The electrodeposited nickel on Glassy Carbon (GC-Ni) electrode was fabricated via electrodeposition of nickel from $NiSO_4.6H_2O$ 10 Mm (where was dissolved in H_2SO_4 0,1 M), then using potential at -1,2 V vs Ag/AgCl. Electrodeposition was held at the potential in 300 (GC-Ni5m) and 600 seconds (GC-Ni10m).

After the deposition was done, GC-Ni5m and GC-Ni10m were then washed in aquabidest and then placed in a KOH 1 M solution for conditioning. The electrodes were cycled between 0,1 and 0,6 V as much as 200 cycles at a scan rate of 200 mVs^{-1}. Then after cycled, GC-Ni5m and GC-Ni10m were characterized with ATR-FTIR and SEM.

Electroanalysis of Formaldehyde

Electroanalysis was used cyclic voltammetry. The electrode modified GC-Ni5m and GC-Ni10m were placed in formaldehyde 0,1; 10; 50; 100; 300 and 500 ppm within KOH 1 M solution. Then cycled with potential scan between 0,1 - 0,6 V, five cycles every concentration and scan rate 200 mVs^{-1}. Third cycles are then used for the analysis of electroanalysis activity and limit detection.

Analysis of Formaldehyde with comparison method

Analysis was used spectrophotometric methods with Schiff's reagent as a coloring agent of formaldehyde. Aqueous formaldehyde 0,1; 10; 50; 100; 300 and 500 ppm with volume 10 µL then mixed with 450 µL of Schiff's Reagent and 40 µL of aquadest. Then the mixed solution and placed in a cuvette and allowed at room temperature for 60 minutes, and then used for standard calibration curves using UV-Vis at 545 nm absorbance wavelength.

### Limit detection and quantification

Limit detection (LOD) was used in cyclic voltammetry and comparison method, determined by linear regression with three times of standard deviation divided by its slope $\left(\frac{3 \times S_{y/x}}{Slope}\right)$ in each standard calibration curve, while the limit of quantification (LOQ) determined by the formula $\frac{10 \times S_{y/x}}{Slope}$.

Results and Discussion

Electrodeposition and Conditioning

The electrodeposition process produced a metallic shiny layer, covering the glassy carbon surface (Fig. 1 and 4). This layer indicated that nickel was deposited on glassy carbon (Toifur *et al.*,

2017). Nickel layer formed by reduction reaction of $NiSO_4$, with reaction 1;

$$Ni^{2+}_{(aq)} + 2e^-_{(aq)} \longrightarrow Ni_{(s)} \quad (1)$$

$$2H^+_{(aq)} + 2e^-_{(aq)} \longrightarrow H_{2\,(g)} \quad (2)$$
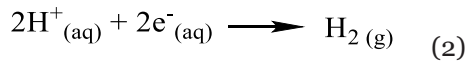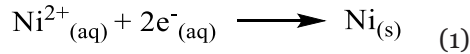
Gaseous Hydrogen was formed during the nickel layer formed (reaction 2), the bubble gas will contribute to forming pores of the nickel layer. Theoretically, nickel layer GC-Ni5m has thickness and mass of 0,144 mm and 9,12 µg, while GC-Ni10m has 0,288 mm thickness and 18,24 µg mass.
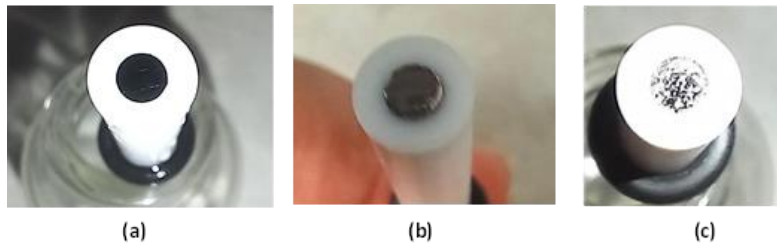

(a) (b) (c)

Figure 1 The difference of Glassy carbon electrodes surface (a) GC, (b)GC-Ni5m, and (c) GC-Ni10m

The conditioning process will activate the nickel layer, form the beta nickel hydroxide from the crystalline layer (Trivedi *et al*., 2018) with reaction 3-5;
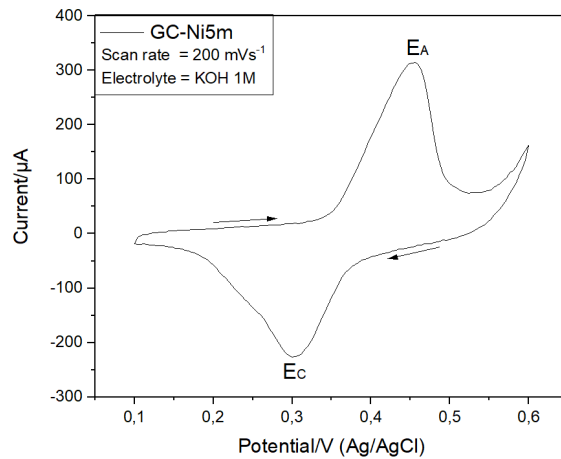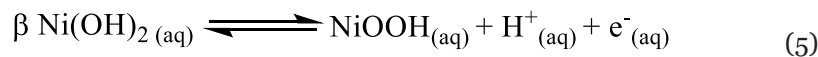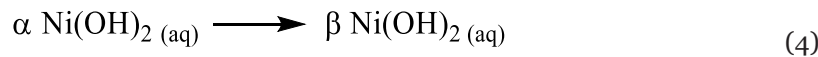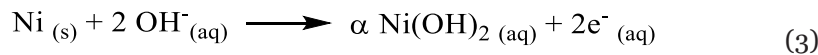

Figure 2 Cyclic Voltammogram when conditioning process

$$Ni_{(s)} + 2\,OH^-_{(aq)} \longrightarrow \alpha\,Ni(OH)_{2\,(aq)} + 2e^-_{(aq)} \quad (3)$$

$$\alpha\,Ni(OH)_{2\,(aq)} \longrightarrow \beta\,Ni(OH)_{2\,(aq)} \quad (4)$$

$$\beta\,Ni(OH)_{2\,(aq)} \rightleftarrows NiOOH_{(aq)} + H^+_{(aq)} + e^-_{(aq)} \quad (5)$$

The formation of beta nickel hydroxide will occur in three steps. First, nickel crystallin turns into alpha nickel hydroxide when potential stepped at -1,5 until -0,7 V vs. Ag/AgCl (not recorded in voltammogram) (Reaction 3). Second, alpha nickel hydroxide turns into beta nickel hydroxide while potential stepped at -0,7 until 0 V vs. Ag/AgCl (not recorded in voltammogram) (reaction 5). Third, beta nickel hydroxide will turn into nickel oxyhydroxide (Reaction 5) when a new peak (E_A in Fig. 2) in voltammogram appears, it indicates that beta Nickel oxyhydroxide fully formed (Medway *et al*., 2006). Peaks E_A is the anodic peak, occur an oxidation reaction and E_C is the cathodic peak when

reduction occurred.

SEM Characterization

Surface morphology of GC-Ni5m and GC-Ni10m are present in Fig. 3. Both of their morphology is seen formed solid nickel layers, but in some parts of both surfaces look to have a crack that can function as a pore. The surface of GC-Ni5m (Fig. 3a), has more cracks and looks deeper than GC-Ni10m (Fig. 3b), which has more crackless and more homogenous surfaces. The cracks on its surface indicate when the electrodeposition process was less controlled (because without the stirrer process), it will create the gradient concentration of electrolyte on the nickel surface. The SEM image of GC-Ni10m is looking brighter, indicate has more conductive. From this characterization, known that the GC-Ni5m has a larger surface area and GC-Ni10m has more conductive.
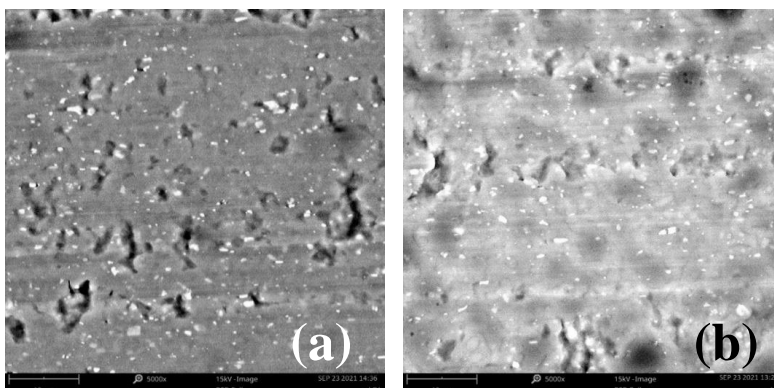

Figure 3 Surface morphology of (a) GC-Ni5m and (b) GC-Ni10m with SEM Characterization

ATR-FTIR Characterization

Infrared characterization was used Screen-printed carbon electrodes are present in Fig. 4. Spectra of GC-Ni5m and GC-Ni10m have several new peaks than GC spectra. The black dotted line Fig 4, shows a new peak in wavenumber of 3400 cm^{-1} indicates stretching and vibration of Hydroxyl group characteristic, followed by peaks of 1650 cm^{-1} and 1080 cm^{-1} (Nandiyanto *et al.*, 2019). Sharp peaks in 1650 cm^{-1} indicate that the hydroxyl group adsorbed on Nickel surfaces (Shangguan *et al.*, 2011) and there is a change of hydroxyl concentration on electrodes when the formation of Ni-OH begins (Wang *et al.*, 2018).
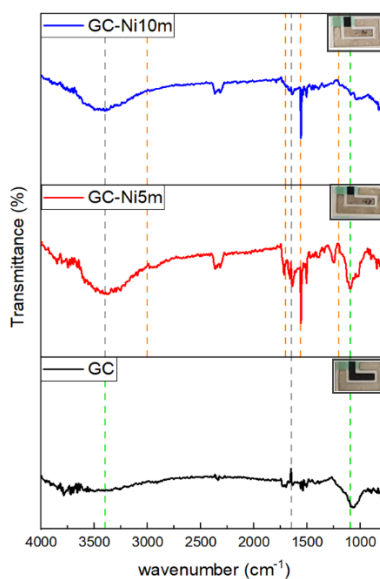

Figure 4 ATR FTIR Characterization of GC, GC-Ni5m, and GC-Ni19m

Besides that, some peaks that appear in GC-Ni5m and GC-Ni10m are shown in the orange dotted line, which indicated the carbon electrodes have been damaged by the acidic solution during when electrodeposition process. The strong acidic electrolyte can break the graphite chain in electrodes and produce the new layer which has some groups like C=O (1644-1700 cm^{-1}), C-H (3000 cm^{-1}), C=C (1563 cm^{-1}), C-C (1080-1200 cm^{-1}) (Yi $et\ al.$, 2017), and other than that, there are the green dotted lines shown peaks in wavenumber of 1094 cm^{-1} in all spectra and there some little peaks -OH in GC spectrum, indicate there some adhesive agent from its electrodes was detected like PVA (Sudhamani $et\ al.$, 2003). Because of that, we used the Glassy Carbon electrode which has harder and inert than the usual carbon electrodes.

Electroanalysis of formaldehyde
Reaction mechanism
The mechanism of electroanalysis reaction can be known by comparing between voltammogram without and with formaldehyde, present in Fig 5.
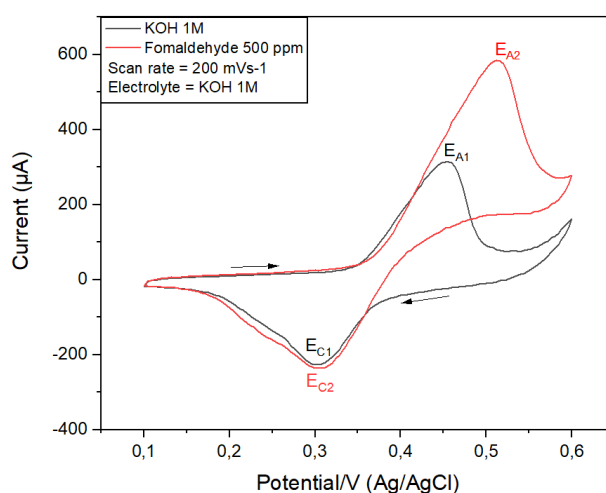

Figure 5 Comparison cyclic voltammograms between Formaldehyde 0 ppm (black) and 500 ppm (red)

Voltammogram electroanalysis of formaldehyde can be identified to two regions when oxidation process, when potential stepped at 0,1 – 0,35 V and 0,35 – 0,6 V. The cyclic voltammogram of KOH (black curve), overall describe adsorption -OH groups and formation of NiOOH (in E_{A1} peaks) which has lower of potential and current intensity from cyclic voltammogram in formaldehyde (red curve) (Hamdan $et\ al.$, 2011). The cyclic voltammogram of formaldehyde (red curve), has a slope at 0,1 - 0,3 V which interpretation that formaldehyde oxidation is sustained by the involvement of adsorbed -OH group (Hamdan $et\ al.$, 2011). After that when potential stepped at 0,35 – 0,6 V, there appeared the E_{A2} peak which has two times higher than E_{A1} in current intensity. This higher peak is the interpretation that oxidation formaldehyde occurs after NiOOH is fully formed at potential 0,46 V (Trivedi $et\ al.$, 2018).

Besides that, in cathodic peaks there are similar peaks between E_{K1} and E_{K2}, it can be known that in formaldehyde electroanalysis there is only NiOOH reduction to $Ni(OH)_2$ without analyte reduction.
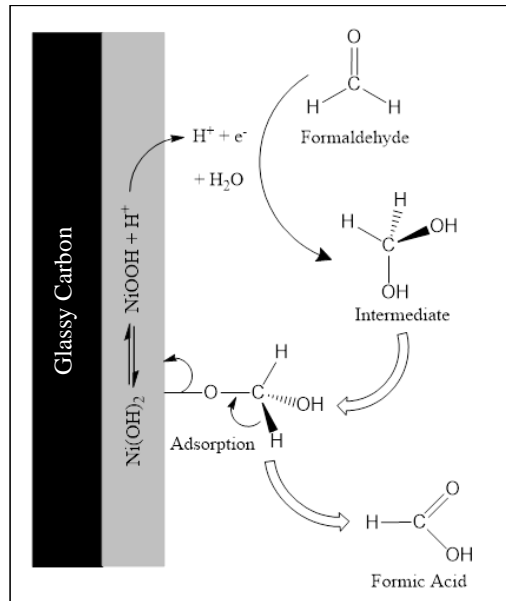
Figure 6 The reaction mechanism illustration of formaldehyde electroanalysis by a nickel layer

The oxidation of formaldehyde will produce formic acid (Fig 6). Oxidation started by forming Ni^{3+} from Ni^{2+}, then formaldehyde will be oxidated by Ni^{3+} and produce an intermediate product which directly adsorbed on the nickel layer and then will be oxidated again to produce the last product (formic acid) (Fleischmann *et al.*, 1971). When potential stepped back to form reduction, Ni^{3+} will be reduced to Ni^{2+} and the analyte will be desorbed but will not be reduced.

Formaldehyde identification

Electroanalysis of formaldehyde with various concentrations produces an increasing peak in anodic peaks consistently, when the concentration of formaldehyde was increased (Fig. 7). When there is more formaldehyde concentration, then more current is generated from the transfer of electrons through oxidation reactions.
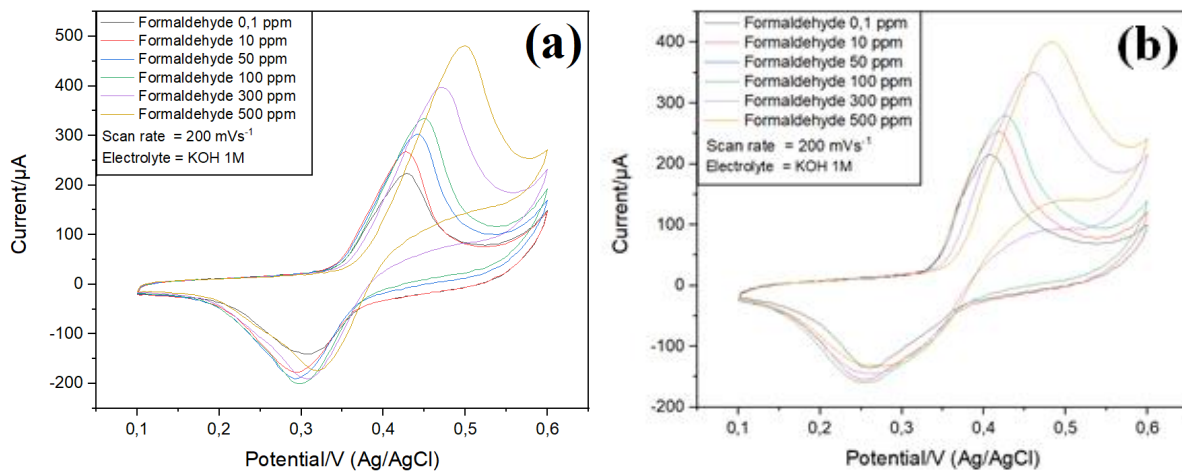

Figure 7 Cyclic voltammograms (a) GC-Ni5m and (b) GC-Ni10m in formaldehyde various concentration

Besides that, there is a potential shift positively when formaldehyde concentration was increased. The potential shift can be described by Nernst's equation Eq.1 (Elgrishi *et al.*, 2018).

$$E = E_{\frac{1}{2}} + \frac{RT}{F} \ln \frac{[Ni^{3+}]+[HCOOH]}{[Ni^{2+}]+[HCOH]} \quad \text{(Equation 1)}$$
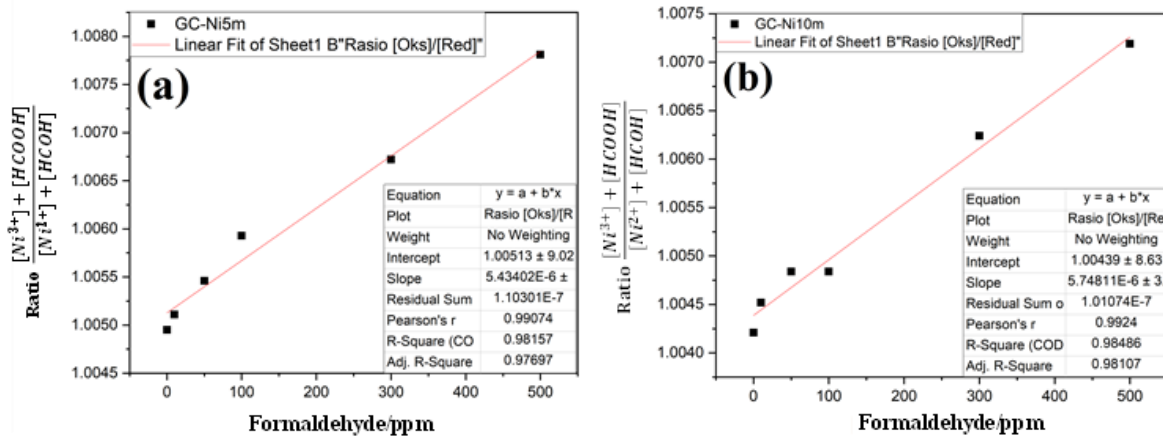

Figure 8 Relationship between oxidation and reduction ratios with increasing potential in formaldehyde at various concentrations (a) GC-Ni5m and (b) GC-Ni10m

The potential is directly proportional to $E_{1/2}$ and the concentration of an oxidated analyte. When there is a more oxidated analyte, the potential will be more positive. From Nernst's equation, we have determined the relationship between oxidation and reduction ratio with formaldehyde concentration (Fig. 8), oxidation ratio would be increased when the concentration of formaldehyde was increased.

Comparison of GC-Ni5m and GC-Ni10m

Both cyclic voltammograms (Fig. 7) were seen the same in the determination of formaldehyde, but both cyclic voltammograms would look different when compared. Fig. 9 presents the comparison of both in lowest concentration (Fig. 9a) and the highest concentration of formaldehyde (Fig. 9b).
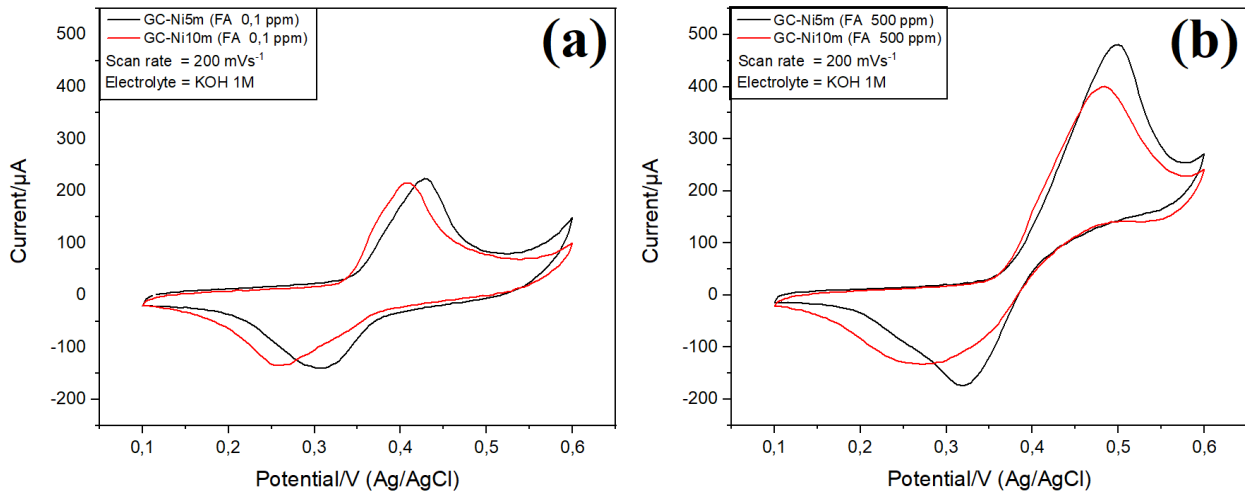
Figure 9 Comparison of GC-Ni5m/black and GC-Ni10m/red cyclic voltammograms in (a) 0.1 ppm formaldehyde and (b) 500 ppm formaldehyde

The difference between both voltammograms is in current intensity and potential shift of anodic peak and cathodic peak. The difference of potential in both E_A is around 0,3 V in lowest concentration and 0,2 V in highest concentration. Besides that, the current intensity has a different response, in both of E_A have differential around 8 μA in lowest concentration and 80 μA in highest concentration. The difference between both cyclic voltammograms is caused by their resistivity properties. Resistivity is a

tendency of its nickel layer to inhibit the flow of electric current provided by the electrode, which is in contrast to its conductivity (Safitri *et al.*, 2014). Resistivity is very influential on the area and thickness of the nickel layer, the thicker layer has lower resistivity (Toifur *et al.*, 2017).

GC-Ni10m has properties thicker than GC-Ni5m, causing GC-Ni10m to have higher conductivity and lower resistivity. Theoretically, GC-Ni10m has resistivity 1.078 Ω.m while GC-Ni5m is 1.704 Ω.m. By its properties, GC-Ni10m could oxidate formaldehyde faster (occurs in lower potential) than GC-Ni5m as evidenced on cyclic voltammograms (Fig. 9). The higher conductivity property of GC-Ni10m was also proved by SEM characterization (Fig. 3).

Detection limit and Quantification
Electroanalysis of Formaldehyde

Cyclic voltammograms of determination formaldehyde with GC-Ni5m (Fig. 7a) and GC-Ni10m (Fig. 7b) were then used to make the standard calibration curves for determining its LOQ and LOQ from its E_A peaks. The linear range was divided into two ranges; low concentration (0,1 - 50 ppm) and high concentration (50 – 500 ppm). The regression linear then calculated from curves of current intensity vs. concentration of formaldehyde and generated the limit detection of GC-Ni5m is 33,17 ppm (low concentration) and 49,76 ppm (high concentration), then the Quantification limit is 110,6 (low concentration) and 165,88 ppm (high concentration) (Fig. 10).
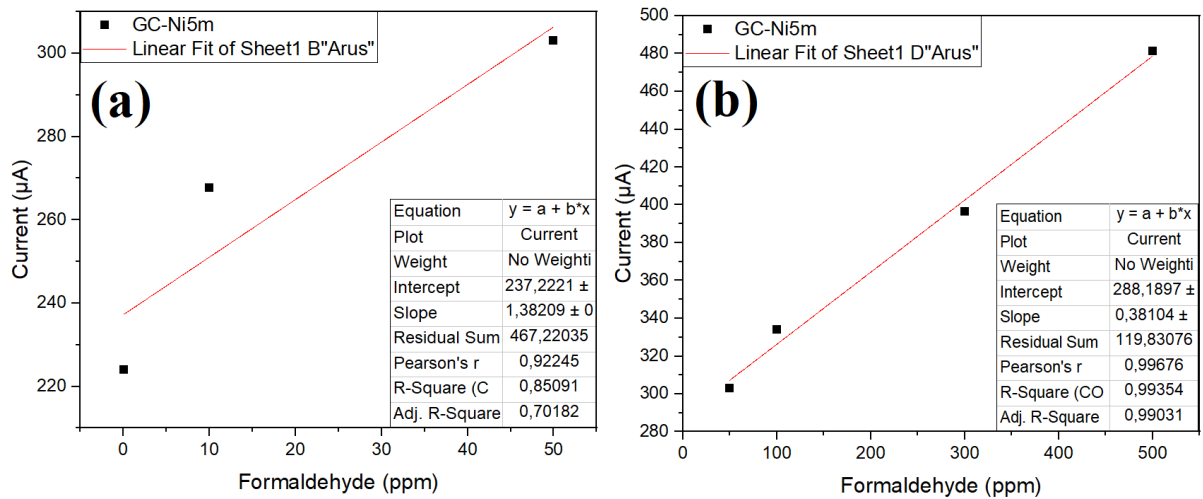

Figure 10 Linearity of cyclic voltammogram GC-Ni5m (a) low concentration and (b) high concentration

Detection limit of GC-Ni10m is 35,86 ppm (low concentration) and 69,94 (high concentration), then the quantification limit is 119,55 (low concentration) and 233,14 (high concentration) (Fig. 11).
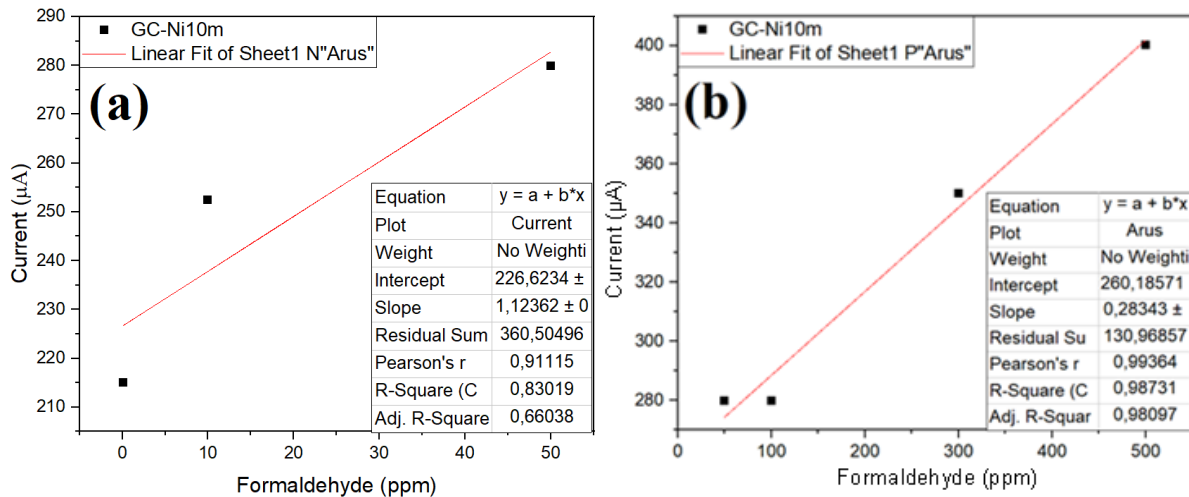
Equation	y = a + b*x
Plot	Current
Weight	No Weighti
Intercept	226,6234 ±
Slope	1,12362 ± 0
Residual Sum	360,50496
Pearson's r	0,91115
R-Square (C	0,83019
Adj. R-Square	0,66038

Equation	y = a + b*x
Plot	Arus
Weight	No Weighti
Intercept	260,18571
Slope	0,28343 ±
Residual Su	130,96857
Pearson's r	0,99364
R-Square (C	0,98731
Adj. R-Squar	0,98097

Figure 11 Linearity of cyclic voltammogram GC-Ni10m (a) low concentration and (b) high concentration

UV-Visible analysis

Schiff's reagent was used in this analysis, with used same concentrations in electroanalysis. Then by using absorbance vs. concentration of formaldehyde, the standard calibration curves were determined. Then used same linear range, divided into two ranges; low concentration and high concentration (Fig. 12). Detection limit from UV-Vis Schiff's reagent is 17,8 ppm (low concentration) and 106,66 (high concentration), then quantification limit is 59,65 (low concentration) and 355,53 (high concentration).
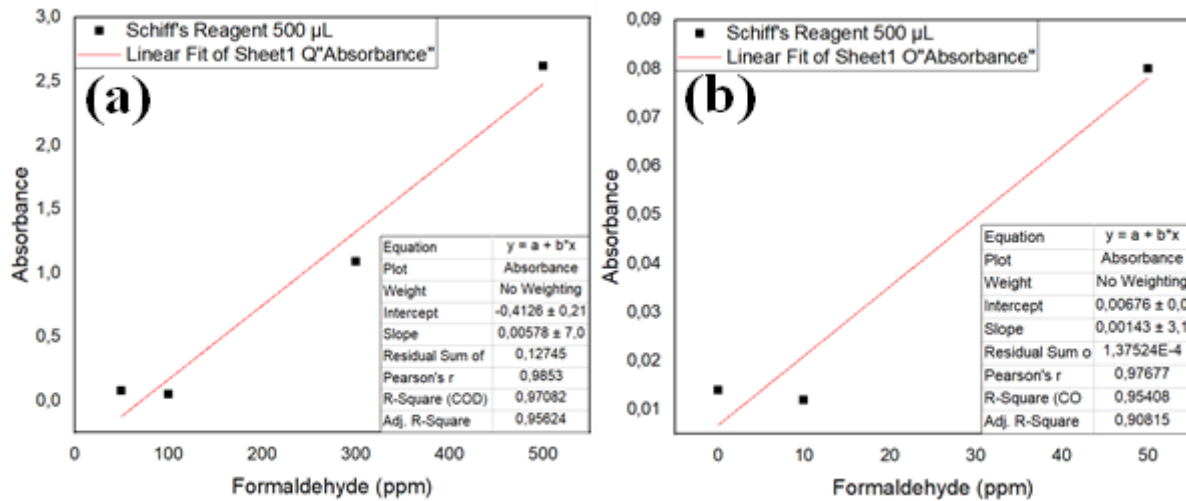

Equation	y = a + b*x
Plot	Absorbance
Weight	No Weighting
Intercept	-0,4126 ± 0,21
Slope	0,00578 ± 7,0
Residual Sum of	0,12745
Pearson's r	0,9853
R-Square (COD)	0,97082
Adj. R-Square	0,95624

Equation	y = a + b*x
Plot	Absorbance
Weight	No Weighting
Intercept	0,00676 ± 0,0
Slope	0,00143 ± 3,1
Residual Sum o	1,37524E-4
Pearson's r	0,97677
R-Square (CO	0,95408
Adj. R-Square	0,90815

Figure 12 Linearity of UV-Vis Schiff's reagent method (a) low concentration and (b) high concentration

Comparison of electroanalysis and UV-Visible methods

The limit of detection and quantification results in this paper is bigger when compared with previous research by Trivedi et al (while has 0,33 ppm of detection limit) or other similar research, this can be caused by several factors that influence, such as a homogenous factor of electrolyte during analysis and its long linear range. Nevertheless, these electroanalysis methods can still be compared with UV-Vis Schiff's reagent methods in this research, because it still uses the same linear range.

Comparison based on detection limit and quantification can be concluded that in the low concentration range of GC-Ni5m, GC-Ni10m and Schiff's reagent could detect under 50 ppm. Whereas in high concentration, GC-Ni5m and GC-Ni10m could detect under 100 ppm, while Schiff's reagent

has a limit detection of 106 ppm. Quantification limit from all methods has a limit above 100 ppm, except Schiff's reagent in low concentration.

If we refer to a maximum level of formaldehyde in foods, according to the European Food Safety Agency standard, the maximum level is 100 ppm (BPOM RI, 2019). The presence of formaldehyde concentrations can still be tolerated because formaldehyde is often found as a by-product of metabolic reactions found naturally in several types of animals or plants, although in small concentrations. So that it can be concluded, the GC-Ni5m and GC-Ni10m methods can be used as formaldehyde detectors with small concentrations and can detect below 100 ppm. While the UV-Vis method with Schiff's reagent in low concentrations can detect below 100 ppm and can be calculated by quantification.

However, each method has advantages and disadvantages. Such as Schiff's reagent is not recommended to do in food samples analysis directly, but have to do through the purification process from organic matrixes. Schiff's reagent was known to react with sucrose, starch, and other glucose and some organic compounds which have aldehyde groups. Whereas electroanalysis methods GC-Ni, the current response is not only from formaldehyde response but there is the current response from nickel oxidation and adsorption-desorption of electrolyte compounds which can affect its linearity. Besides that, the nickel layer is possible to react with nitrogenous molecules to form covalent bonds.

Conclusion

Nickel has been successfully deposited on a Glassy Carbon electrode. The variation of deposition time 300 and 600 seconds will affect the morphology of the nickel surface layer and would affect to the activity of formaldehyde electroanalysis. GC-Ni10m could oxidate formaldehyde faster (occurs in lower potential) than GC-Ni5m, caused by resistivity which is inversely proportional to the nickel thickness. GC-Ni5m has a larger surface area than GC-Ni10m caused its heterogeneous surface morphology and some cracks which could be pores. The current intensity in cyclic voltammogram is the response from the electron transfer process of nickel oxidation, and then formaldehyde oxidation. The potential shift of anodic peaks could be predicted and described by Nernst's equation. Deposited nickel on carbon electrode with using strong acid electrolyte could damage its graphite bond.

The limit of detection and quantification are calculated using the anodic peak of the cyclic voltammogram. The detection limit in low concentration of GC-Ni5m is 33.17 ppm which is smaller than GC-Ni10m of 35.8 ppm. The high concentration of GC-Ni5m is 49.7 ppm, then GC-Ni10m is 69.9 ppm. While the quantification limit in low concentration of GC-Ni5m of 110.5 ppm is smaller than GC-Ni10m of 165.8 ppm, in the high concentration of GC-Ni5m of 165.8 ppm and GC-Ni10m of 233.14 ppm. All three methods can be used as a method of analyzing formaldehyde. In the low concentration range, Schiff's reagent can detect formaldehyde the best, while in the high concentration range, GC-Ni5m can detect formaldehyde the best.

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