QCM SENSOR SENSITIVITY ANALYSIS OF SILVER ELECTRODES COATED WITH LIPID MEMBRANE OLEYL ALCOHOL TOWARD NaCl AND HCl

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ABSTRACT

One of the sensors, which is currently being developed is the QCM sensor. The QCM sensor is a sensor that utilizes the frequency change to detect a change in mass due to a test substance. The use of a QCM sensor includes other forms of electronic tongue sensor that can distinguish five basic flavours on the tongue. QCM sensor can also be varied electrodes using various lipid membranes such as electronic tongues to increase sensor sensitivity. This research aims to determine the sensitivity of the QCM sensor before and after coated with lipid membrane to NaCl and HCl. The sensitivity of the QCM sensor to NaCl is 1.47 Hz/M for uncoated sensor and 0.63 Hz/M for coated sensor, while the sensitivity of HCl is 4.55 Hz/M for uncoated sensor and 4.93 Hz/M for coated sensor. The difference of the results is caused by the nature of ionization of the compound and the amount of concentration used. The result of the sensitivity research shows that the QCM sensor with Oleyl Alcohol lipid membrane is more sensitive to HCl than NaCl.

Keywords: QCM Sensor; Oleyl Alcohol; Sensitivity; NaCl; HCl

Introduction

Sensor technology has been experienced in very rapid development. Various sensors were created to ease the people activities. Some of them also created to replace the role of organs in the human body in order to avoid harmful materials. Sensors that can replace the functions of human organs include electronic tongue sensors, electronic nose sensors and electronic eyes sensors. The sensors were developed to meet the limitations of the human body.[1]

Human organs that need to be protected and have limitations are the five human senses. One of the five senses that can directly interact with chemicals is a tongue. The human tongue has a threshold in detecting basic tastes and susceptible to damage when exposed to harmful substances. That problem is the reason for assembling electronic tongue sensor. Various sort of electronic tongue sensor have been developed including *Quartz Crystal Microbalance* sensor (QCM).[2]

QCM sensor is made of AT-*cut* quartz crystal pieces. There are electrodes on the upper and lower sides of the sensor as well as holders that connect it to the processor. The working principle of the QCM sensor is it is vibrated by an oscillator so it vibrates stably. Effect of Inverse-piezoelectric works in testing QCM sensors cause deformation and generates an electric field. Oscillation frequency on the sensor is calculated by the frequency counter through the electric field.[2] QCM sensors utilize the change in oscillation frequency value to determine the change in mass substance. This is shown in the Sauerbrey equation as follows [3]:

$$\Delta f = \frac{-C_f f_0^2 \Delta m}{A} \quad (1)$$

The use of QCM sensors is another form of electronic tongue sensor because it can be used for liquid samples. Sensor electrodes

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can also be varied by coating other compounds such as lipid membranes and polymers. This study used the lipid *Oleyl Alcohol* membrane to increase sensor selectivity. The use of these membranes is based on research carried out by Al Jazuly in testing the taste of the tongue using an *e-tongue* sensor.[4]

There are five basic flavours on the tongue; sweet, sour, salty, bitter and savoury taste (umami). This study used NaCl test material to represent the salty taste and HCl to represent the sour taste. Testing salty taste with sensors is needed because the determination of salt quality standards in Indonesia could not be done directly with the human tongue. Acid testing also could not be detected directly by the tongue because strong acids can damage the tongue's organs.[5,6]

In this study, testing of salty and sour taste was carried out by using varied electrode QCM sensor. Electrodes used to test NaCl and HCl are pure silver and coated Oleyl Alcohol lipid membrane layer electrodes. Membrane coating aimed to protect sensor electrodes and increase sensor selectivity. The technique used to coat the sensor is a *spin coating* technique. It is a material coating method using the centripetal force on the material to get a layer that is evenly distributed on the entire surface.[7]

QCM sensor could not be operated without a series of processors. Its processor circuit consists of an oscillator, microcontroller and frequency counter. This study used open-QCM for examination. It is found a micro Arduino as a microcontroller and frequency counter along with an Arduino shield QCM as an oscillator in open-QCM. Open-QCM series was also integrated with the open-QCM 1.2 software that can display the sensor oscillation frequency output in real-time so it is easy to use.[8]

Figure 1. Open-QCM series

Methods

In this study, the data were gained through three stages; *preparation, sample testing,* and *data processing stage*. Preparation stage included membrane coating and sample measurement. Membrane coating on the surface of the QCM sensor electrode uses the spin coating method. *Oleyl Alcohol* lipid membrane is made of three main components; 3% lipids, 32% PVC and 65% plasticizers.[9] QCM sensor that is used has crystal resonator with a diameter of 8.90 mm, HC-49/U holder, and silver electrode with a diameter of 5.1 mm.

Figure 2. QCM HC-49/U Sensor

Measurement of sample test using two methods: *dissolution* and *dilution*. Dissolution was carried out on NaCl crystal using equation (2). The amount of NaCl concentration tested was 20 concentrations of 100 mM - 2000 mM at intervals of 100 mM. Dilution method was carried out on 32% concentrated HCl samples by using equation (3). There were 10 concentrations of HCl tested between 100-550mM. HCl concentration interval was 50 mM. The amount of HCl concentration is not the same as NaCl because of the nature of HCl is a

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strong acid. A too-high HCl testing in concentration can cause corrosion on QCM holder.

$$M = \frac{m}{Mr} \times \frac{1000}{V} \quad (2)$$

$$V_1 . M_1 = V_2 . M_2 \quad (3)$$

The sensor testing phase carried out by testing the sensor's basic frequency. Basic frequency is the frequency on the sensor before being subjected to the sample. Basic frequency testing aims to control the sensor when changing the concentration of the test sample. Both types of sensors are vibrated for five minutes with five times repetitions. Then, data from basic frequency is averaged to become a reference for further testing. Testing of NaCl and HCl samples was carried out after the basic frequency is determined. Samples were dropped on the surface of the QCM sensor as much as 100 µL using a micropipette drop. The duration of testing is five minutes with five repetitions. Each repetition produces 300 data. Analysed data is the last 200 data because the data is a stable state of the sensor.

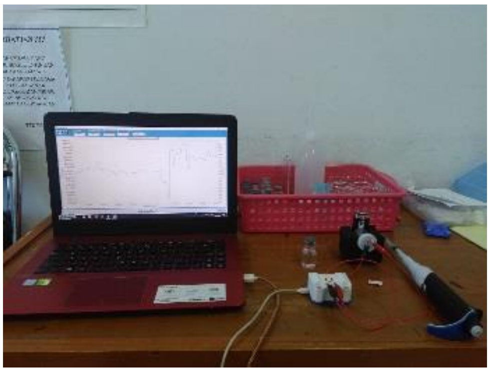

Figure 3. QCM sensor testing process

Afterwards, oscillation frequency data obtained is averaged in the last 200 data and analysed by sensor sensitivity. The data processing stage is done using the Origin-Pro 2017 software. Sensor sensitivity is obtained by linear regression of the relationship between sample concentration and oscillation frequency. Linear regression analysis will show slope, intercept and analysis of errors in the data. Determination of sensor sensitivity aims to determine the sensor's ability to detect changes in the test material.

Result and Discussion

Sensitivity is one of the characteristics that sensor users must know. Sensitivity value is a value that shows the ability of the sensor response when a sample changes are tested. Sensor sensitivity analysis was performed by linear curve regression analysis of the relationship between sample concentration and sensor oscillation frequency. Linear regression is determined by the transfer function of a curve shown in equation (4).

$$y = a \pm bx \quad (4)$$

Sensitivity value is shown in the value b in equation (4). The value b shows the slope curve. Sensor sensitivity towards input changes is indicated by the slope curve value. Linear regression is performed on the curve of the sensor work area. Work area compared between the two sensors must be equalized. Sensitivity analysis of the QCM sensor on NaCl testing is at a concentration of 1000 mM-2000 mM, while the HCl test is at a concentration of 250-550 mM.

Linear regression results of NaCl testing with pure silver QCM sensor (y = 1.40553E7 - 1468.96871x) as in figure 4. The equation shows that the sensor sensitivity value is 1468.96 Hz / mM. The regressed work area adapts to the sensor work area with the membrane because the ratio must be the same.

There was a decreasing on Sensor oscillation frequency value along with increasing sample concentration. Oscillation frequency has increased at a concentration of 1100 mM and 1900 mM, yet it is back to decrease in the next concentration. So, the slope is higher than coated QCM sensor. Sensor output values in HCl testing with uncoated membrane are in the frequency range between 12.6 MHz-10.8 MHz changes in sensor output indicate that the sensor can respond to changes in the concentration of the tested sample.

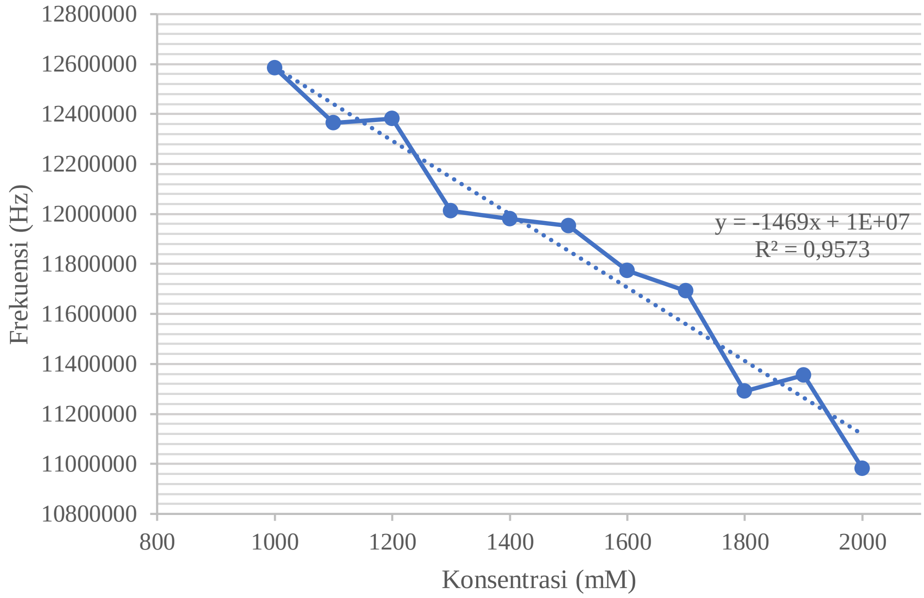

Figure 4. Analysis of uncoated QCM Sensor Sensitivity on HCl

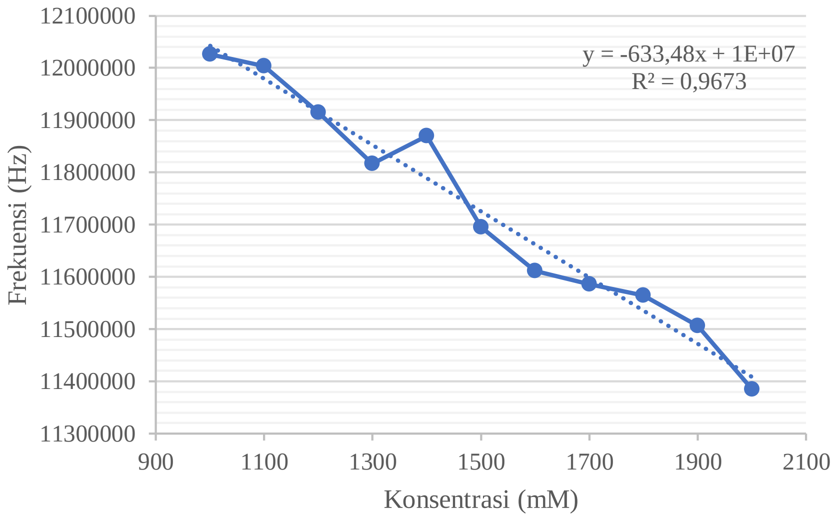

Figure 5. Analysis of Coated QCM Sensor Sensitivity on NaCl

Linear regression curve of coated QCM sensor test results in NaCl sample is shown in Figure 5. Its equation is y = 1.26753E7 - 633.48473x. Sensitivity value of the regression curve is 633.48 Hz / mM. Coated QCM sensor sensitivity in Figure 5 is smaller when compared to the uncoated one.

Figure 6 shows the results of sensitivity analysis of pure silver QCM sensor electrodes in HCl. Linear regression equation obtained is y = 1.37025E7 - 4545.00315x. Sensitivity analysis of sensors in HCl testing showed very different results. Sensitivity values obtained are much greater than NaCl.

The sensitivity of the uncoated QCM sensor in HCl testing is 4545 Hz / mM. There is a difference in sensitivity values of NaCl and HCl testing was caused by differences in the concentration of the sample used. NaCl concentration tested was greater than HCl concentration so that the sensor response was lower than HCl.

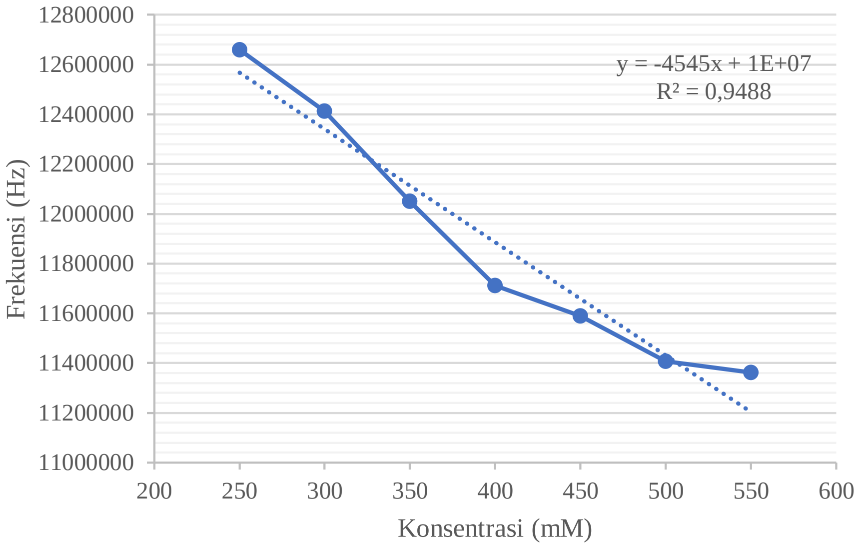

Figure 6. Analysis of uncoated QCM Sensor Sensitivity on HCl

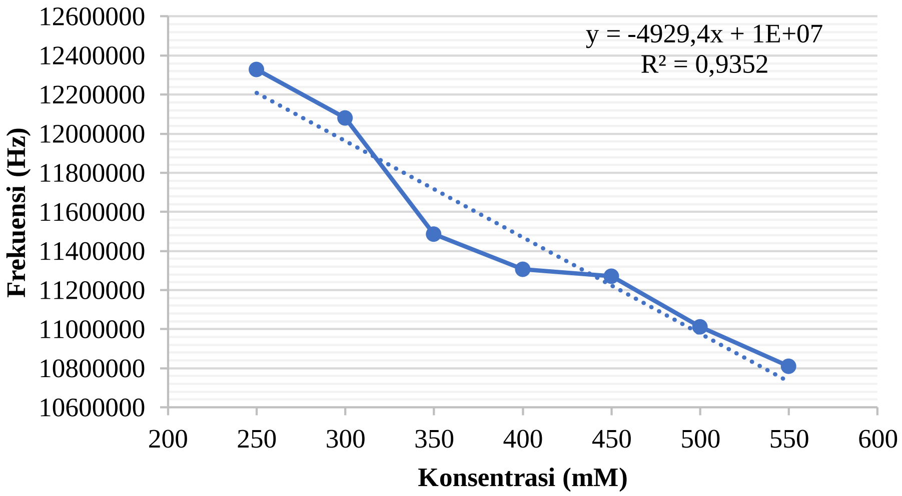

Figure 7. Analysis of Coated QCM Sensor Sensitivity on HCl

Coated QCM sensor testing in HCl has a working area between concentrations of 250 mM-550 mM. Regression analysis of linear work area curves is shown in Figure 7. Linear regression equation obtained is y = 1.34423E7 - 4929.41032x. Sensor sensitivity that is obtained from HCl testing was 4929.4 Hz / mM. This value is higher than the uncoated QCM sensor. Then, it is gained overall data from the sensor sensitivity testing analysis. It is shown in table 1.

Table 1. Result of Sensitivity Analysis

Electrode Sensor	**NaCl**		**HCl**	
	Sensitivity (Hz/M)	**R^2**	**Sensitivity (Hz/M)**	**R^2**
Silver (Pure)	1.47	0.96	4.55	0.95
Coated Silver	0.63	0.98	4.93	0.93

Coated QCM sensor sensitivity is higher on HCl testing. It caused by protonation interactions occurs between membranes and HCl. Protonation interaction is the binding ability of protons from a compound binding to other compounds. Oleyl alcohol lipid membrane has a chemical structure $C_{18}H_{36}O$. The structure is a long hydrocarbon chain with an outer functional group in the form of OH. The C18H36O chain is shown in Figure 8.

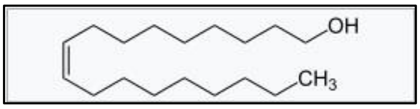

Figure 8. Chain of Oleyl Alcoholic Hydrocarbon

Protonation interactions are caused by OH groups that change to O- and H + when they meet a sample test. Protons from NaCl and HCl will be bound by O-ions so that they are absorbed by the membrane and cause changes in the sensor mass. The change in mass causes changes in the frequency of sensor oscillations. Oscillations sensor frequency is decreased along with the increasing of concentration. The greater the concentration of the test sample, the greater the mass bound by the membrane and the more difficult to vibrate. This causes the number of oscillation sensor frequencies to become inversely proportional to concentration sample. Sensitivity value of coated QCM sensors on HCl is higher than NaCl due to the differences in concentration and ionization level of compounds. HCl is a strong acid which is very reactive when interacting with oleyl alcohol lipid membranes, in addition the concentration of HCl is smaller than NaCl so that it is more easily vibrated by the sensor.

Conclusion

In NaCl testing, Uncoated QCM sensor sensitivity is higher than the coated ones. Meanwhile, in HCl testing, it is found that coated QCM sensor sensitivity is higher than the uncoated one because of the presence of strong acid ions in HCl which are more reactive to the membrane. It caused by ionization properties of HCl which is more reactive to lipid oleyl alcohol membrane than ionization properties of NaCl. HCl concentration is smaller than NaCl so that HCl is more easily vibrated by the sensor. This study showed that lipid oleyl alcoholic membrane on the QCM sensor is more appropriate for testing HCl rather than NaCl. Coated QCM sensor sensitivity for HCl testing is three folds higher than NaCl testing with a response time of 15 s.

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