Influence of the liquid injection hole to ripple frequency of the QCM sensor

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Abstract. The liquid injection is one of the crucial roles in the used of QCM sensors in a liquid application. Liquid sample injection should be controlled. As the liquid injected onto the QCM sensor surface using peristaltic pump, a short pressure pulse exists. The short pulse affect the stability of the resonance frequency of the QCM sensor. The pulsation flow of the peristaltic pump leads to a ripple resonance frequency of the QCM sensor. Resonance frequency measurement of the QCM sensor in the reaction cell injected using the peristaltic pump has been measured. Different injection holes size was made to observe the effect to the sensor stability. The result showed that frequency of the QCM sensor has a ripple frequency as the liquid injected using the peristaltic pump. It was observed that bigger injection hole at the exit flow resulted in a smaller ripple frequency. Further investigation is required to get the smallest ripple frequency during the liquid injection using the peristaltic pump.

1. Introduction
The Quartz Crystal Microbalance (QCM) has a broad application range, including chemical and biosensors. The resonance frequency shifts of the quartz crystal were caused by some interaction of the sensor with its environment [1]. The change in frequency is proportional to the increase in mass on the surface as long as the mass is firmly attached to the deformation of the crystal oscillation. Due to several advantages of QCM sensors such as high sensitivity, high resolution, and low cost, they have been widely used in the fields of chemistry, biology, physics, and medicine, especially in the analysis of gas or liquid composition [2]. Also, QCM has a high sensitivity to be able to detect changes in mass in the order of micrograms to nanograms. This high sensitivity causes research on QCM sensors in a variety of applications increasingly rapidly, especially in its application as a biosensor [3].

In order to study the interactions of a biospecific pair of molecular, first, one counterpart need be immobilized on the sensor surface [4]. In its use as a biosensor, the sample in water solution is injected to the sensor surface. Therefore, the liquid injection system is important. In previous studies, it was known that the flow rate effect of the syringe pump injection system affected the frequency response of the QCM sensor [5]. However, there were some shortcomings in the syringe pump; among others, the flow rate range was limited. Besides, the syringe pump is unable to flow the liquid to the sensor surface continuously. In this study, a peristaltic-based pump is used. Peristaltic pumps are used because these pumps can flow liquid continuously. Peristaltic pumps are also able to produce a higher flow rate range.

QCM sensor works in general as part of an oscillator circuit [6]. One surface of the sensor directly comes in contact with the liquid containing the biomolecule sample [5] or other chemical substance to
be detected. The mass of the biomolecule sample or the substance deposition on the sensor surface affects the resonance frequency of the sensor [7]. The Sauerbrey equation described the frequency change to the mass change on top of the sensor surface [8]. While in contact with liquid, the resonance frequency of the sensor changes due to the viscosity and density of the liquid. Kanazawa and Gordon showed the relation to the resonance frequency to the density and viscosity of the contacting liquid [9]. However, due to the thin plate of the QCM sensor, for example a 10 MHz sensor has a thickness of 167 µm, pressure change caused by liquid flow fluctuation may also affect the sensor resonance frequency [10].

The peristaltic pump sucks up liquid using a vacuum technique created by cyclic compression movements along with its flexible hose. Changing the rotation rate of the peristaltic pump motor changes the flow rate [11]. The rotation of the peristaltic pump produces a cyclic compression along the flexible hose, and therefore change the liquid pressure. The change of the liquid pressure propagates to liquid on the QCM sensor surface. Therefore, the QCM sensor also experiences a pressure fluctuation. Depending on the pressure change, it may affect to the QCM vibration. This work shows the effects of the flow rate of the peristaltic pump to the stability of the resonance frequency of the QCM sensor in contact with water.

2. Experimental

In this study, a liquid injection system in the form of a peristaltic-based pump is used. The movement of the stepper motor was assisted by a TB6600 motor driver which was controlled by an Arduino Nano microcontroller. The stepper motor used was a bipolar stepper motor with 200 steps per 360 degrees which in this study used a micro-stepping mode (1/32) to obtain more accurate results. The retrieval of the QCM sensor response data was carried out in the form of a change in the resonance frequency of the observation time. Data retrieval was done by flowing some distilled water continuously on the surface of the QCM sensor with a flow rate of 0.5, 1, 1.5, 2, and 2.5 µl/s for each reaction cell. There were 3 reaction cells with the different injection hole size i.e 1, 1.5, and 2 mm which was shown at Figure 1.

![Figure 1. Reaction cell with the hole injection size of (a) 2mm, (b) 1.5 mm, and (c) 1 mm](image)

Figure 2 shows the experimental setup of the experiment. One end of the peristaltic pump was placed in an open-air water container, and the other end was inserted into the QCM reaction cell. The QCM sensor was placed on a cell construction which was connected to an oscillator circuit. The resonance frequency of the sensor was recorded in every second using a frequency counter. The data was displayed as a sensogram. In the same time the frequency data was stored for further processing.
3. Result and Discussion

Testing the response of the QCM sensor was carried out by flowing water onto the surface of the QCM sensor continuously. The test was carried out by flowing the water at a flow rate of 0.5, 1, 1.5, 2, and 2.5 \( \mu l/s \) for each reaction cell with the size of the injection hole are 1, 1.5, and 2 mm. Before the water was injected into the reaction cell where the QCM sensor was inserted, the frequency of the sensor was recorded. After a constant resonance frequency in contact with air was achieved \( (f_0) \), the water was pumped to the reaction cell until the sensor surface was entirely covered with water. A new resonance frequency was reached. The recording was done by injecting water continuously for 3 minutes then the pump is stopped for 2 minutes. This is repeated for 5 cycles for 1 flowrate, then the same cycle is continued with a different flowrate.

Figure 3 shows the frequency change of the sensor to the initial frequency in contact with air \( (f_0) \). The frequency is the frequency difference between the resonance frequency at the measuring time to the initial frequency. It can be seen that the resonance frequency of the sensor change around -6KHz. Higher liquid injection hole size leads to a bigger frequency change.
Figure 3. Lag time when the sensor surface is in contact with air until when the entire sensor surface has been covered with water for 3 variation of hole injection size with the flowrate (a) 0.5 µl/s, (b) 1 µl/s, (c) 1.5 µl/s, (d) 2 µl/s, and (e) 2.5 µl/s.

The lag time that occur when the sensor surface is still in contact with air and when the sensor surface is entirely covered with water for flow rates of 0.5, 1, 1.5, 2, and 2.5 µl/s respectively are 54, 23, 17, 15, and 11 second. The time difference was as expected, as bigger flow rate means that the time to fill the same volume is shorter. From the graph the time difference was as expected, as bigger injection hole size means that the time to water come out from the hole is longer. After the surface of the sensor covered with water, the resonance frequency overall is constant.

The next recording is done by injecting water onto the sensor surface using a peristaltic pump with a different flowrate and then the pump is turned off. The process is carried out as many as 5 cycles for each flowrate. Figure 4 shows the injection cycle of the reaction cell with an injection hole size of 2 mm and a flowrate of 0.5 µl/s. Based on Figure 4, during the injection the fluctuated signal is occured. When the water comes out from the injection hole and touches the sensor surface, it changes the resonance frequency due to the pressure applied to the sensor surface. The pressure experienced by the sensor surface due to the continuous rotation of the pump causes the sinusoidal signals. Sinusoidal signals are formed due to repeated vibrations caused by drops of water on the sensor surface. When the pump is stopped, the signal will up slowly to its resonance frequency.
Figure 4. Injection cycle of the reaction cell with an injection hole size of 2 mm and a flowrate of 0.5 µl/s.

The fluctuation of the resonance frequency of the QCM sensor in contact with flowing water pumped using the peristaltic pump with the flowrate of 0.5 µl/s is presented in Figure 5. The fluctuation decreased with an increasing the size of reaction cell injection hole. At 1 mm holes, the ripple frequency peak to peak that occur on average is 14 Hz, while at holes 1.5 and 2 mm are 11 and 8 Hz. The fluctuation could be attributed to the cyclic pressure change as the peristaltic pump head rotated.

Figure 5. The relationship between the ripple frequency peak to peak and observed time with flowrate 0.5 µl/s for the injection hole size of (a) 1 mm, (b) 1.5 mm, and (c) 2 mm.
Residual analysis was applied to the resonance frequency at the fluctuating signal. The residual value of the resonance frequency is bigger at a higher flow rate and smaller injection hole size. Figure 6 shows the ripple frequency dependency on the water flow rate and injection hole size. The ripple frequency at a 1 mm hole with flow rate of 0.5 μl/s is 4.33 Hz, 7.56 Hz at 1μl/s, 7.52 Hz at 1.5 μl/s, 9.08 Hz at 2μl/s and 9.67 Hz at 2.5 μl/s. The ripple frequency at a 1.5 mm hole with flow rate of 0.5 μl/s is 3.66 Hz, 6.52 Hz at 1μl/s, 6.39 Hz at 1.5 μl/s, 9.04 Hz at 2μl/s and 10.6 Hz at 2.5 μl/s. The ripple frequency at a 2 mm hole with flow rate of 0.5 μl/s is 2.61 Hz, 5.41 Hz at 1μl/s, 6.7 Hz at 1.5 μl/s, 7.48 Hz at 2μl/s and 9.36 Hz at 2.5 μl/s.

The graph shows that the ripple frequency of the QCM sensor increased with increasing water flow rate injected using the peristaltic pump and overall decreased with increasing injection hole size. The pressure experienced by the sensor surface is very influential on the sensor frequency response was seen from the size of the ripple frequency that occurs. The smaller ripple frequency causes a more stable sensor response. Therefore it is important to control the water flow rate when the QCM sensor used with the peristaltic pump. Pressure cancelation or a low pass filter needs to be applied to minimize the pressure change caused by the peristaltic pump.

4. Conclusion
The frequency change of the QCM sensor in contact with air to water has the same lag time for each injection hole size. The difference lies in the time when the water begins to drip from the injection hole until the water drips completely onto the sensor surface. Higher injection hole size has a longer time. The pressure fluctuation of the water caused by the peristaltic pump injection mechanism affects the resonance frequency of the QCM sensor. The resonance frequency of the sensor was fluctuated according to the cyclic pressure change caused by peristaltic pump head rotation. Higher flowrate and smaller injection hole size followed by a bigger ripple of the resonance frequency of the sensor. At each injection hole size the fluctuation have constant ripple amplitude but for larger hole size the ripple amplitude is smaller.

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References
[1] N. Mukhin and R. Lucklum, “QCM based sensor for detecting volumetric properties of liquids,” Curr. Appl. Phys., vol. 19, no. 6, pp. 679–682, 2019.
[2] X. Zheng et al., “Sensors and Actuators B: Chemical A fast-response and highly linear humidity sensor based on quartz crystal microbalance,” Sensors Actuators B. Chem., vol. 283,
no. August 2018, pp. 659–665, 2019.

[3] H. Jie, “Technical background, applications and implementation of quartz crystal microbalance systems,” no. September, p. 65, 2006.

[4] X. Li, S. Song, Y. Pei, H. Dong, T. Aastrup, and Z. Pei, “Sensors and Actuators B: Chemical Oriented and reversible immobilization of His-tagged proteins on two- and three-dimensional surfaces for study of protein – protein interactions by a QCM biosensor,” vol. 224, pp. 814–822, 2016.

[5] R. N. Ikhsani, “Design of Low Noise Micro Liter Syringe Pump for Quartz Crystal Microbalance Sensor,” 2018 5th Int. Conf. Electr. Eng. Comput. Sci. Informatics, pp. 598–602, 2018.

[6] K. Jaruwongrungsee, T. Maturos, and P. Sritongkum, “Design and Simulation of Flow Cell Chamber for Quartz Crystal Microbalance Sensor Array,” ECTI-CON2010 2010 ECTI Int. Conference Electr. Eng. Comput. Telecommun. Inf. Technol., no. 1, pp. 548–551.

[7] S. Kurosawa, J. Park, H. Aizawa, S. Wakida, H. Tao, and K. Ishihara, “Quartz crystal microbalance immunosensors for environmental monitoring,” vol. 22, pp. 473–481, 2006.

[8] G. Sauerbrey, “Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung,” Zeitschrift für Phys., vol. 155, no. 2, pp. 206–222, 1959.

[9] K. K. Kanazawa and J. G. Gordon, “Frequency of a Quartz Microbalance in Contact with Liquid,” Anal. Chem., vol. 57, no. 8, pp. 1770–1771, 1985.

[10] E. S. Muckley, J. Lynch, R. Kumar, B. Sumpter, and I. N. Ivanov, “PEDOT:PSS/QCM-based multimodal humidity and pressure sensor,” Sensors Actuators, B Chem., vol. 236, pp. 91–98, 2016.

[11] J. M. Berg, “Peristaltic Pumps,” Science (80-. ), vol. 181, no. 4095, pp. 201–201, Jul. 1973.