A PROPAHOL GAS MEASUREMENT SYSTEM USING A QUARTZ CRYSTAL MICROBALANCE AS A MASS SENSOR

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ABSTRACT

Propanol gas is an alcohol compound classified as a volatile organic compound (VOC). This gas can be classified as air pollution with a harmful impact on human health. There is an urgent need to minimize the health impact by mitigating propanol gas concentration. There is limited information about propanol gas measurement. Therefore, developing a propanol gas measurement device with high sensitivity and selectivity is necessary. Hence, this study developed a propanol gas concentration measurement system based on a bare quartz crystal microbalance. This crystal was placed inside an experimental chamber and exposed to propanol gas. The crystal frequency shift was measured using a frequency counter. The results show that the propanol gas concentration is linearly correlated to the frequency shift resulting in the crystal with a regression coefficient of $R^2 > 0.75$. The system can measure propanol concentrations $< 1 \mu g.L^{-1}$ with a sensitivity of $5 \text{Hz.mg.L}^{-1}$. It can be concluded that a gravimetry-based measurement system using a quartz crystal microbalance has the potential to measure the concentration of propanol gas.

Keywords: air pollution, frequency, propanol, quartz crystal microbalance

1. INTRODUCTION

Propanol gas is an alcohol compound with the molecular formula of C$_3$H$_7$O (Mokoena et al., 2022). Propanol is a toxic volatile organic compound (VOC) that is flammable and volatile. Propanol gas can cause an explosion when exposed to heat (Gad et al., 2021). Propanol is widely found in many sectors, such as power plants (Aburime et al., 2022), diesel engines (Gawale & Srinivasulu, 2020), and even indoors (Samadi et al., 2021). Propanol gas harms health. Exposure to propanol gas in the air that reaches 400 ppm can cause respiratory tract disorders, optic nerves, and irritation of the retina. However, exposure to larger amounts can cause headaches, shock, fainting, and even death (Mokoena et al., 2020; Yin et al., 2020).

Propanol gas can be measured using many techniques, such as a GC-MS or gas chromatography-mass spectrometry (Mylapilli & Reddy, 2020), nanocomposite material (Samadi et al., 2021), and resistivity sensor (Mokoena et al., 2022). A spectroscopy method this technique needs a specific operator and a long analyzing time. GC-MS is well-known as a high-cost device and needs a certain maintenance schematic (Mylapilli & Reddy, 2020). Another technique, the resistance sensor, is categorized as a low-cost device and is not a hand-held device (Mokoena et al., 2022). Moreover, a nanocomposite-based sensor has a limitation in usage and additional chemical treatment and is categorized as a high-cost sensor (Samadi et al., 2021).

For an alternative method, a QCM (quartz crystal microbalance) has the potential to be developed as a gas sensor (Jang et al., 2022). QCM has been widely used for gas sensors due to its high mass sensitivity and low cost (Liu et al., 2022). This sensor has a gravimetry principle with a fluctuating resonance frequency related to the deposited mass onto its electrode surface (Budianto et al., 2022). A gravimetry principle shows that the deposited mass is linearly correlated with the frequency shift (Jang et al., 2022). This sensor is easily developed as a selective sensor and is easily investigated using supporting devices, such as an oscillator and a frequency counter (Zhang et al., 2021). Following the above explanation, this study aims to develop a measurement device for propanol gas. QCM was chosen due to its ease of response analysis and compact dimension and was categorized as a low-cost sensing component (Liu et al., 2022). Thus, the
QCM sensor was tested under different propanol sensors to investigate its performance in sensing propanol gas, such as linearity, measurement range, and sensitivity.

2. MATERIALS AND METHODS

Sensor
This measurement device consists of a bare QCM (Q1) with a fundamental frequency of 5 MHz. This QCM sensor has Ag (silver) electrodes categorized as an AT-cut crystal. The sensor is installed on a sensor-fitting probe and connected to an oscillator and a frequency counter to measure the frequency response \( f \) (Sakti et al., 2019). These components are placed into a sensor box with a dimension of 7.7 x 5.0 x 2.5 cm\(^3\) made of an acrylic box. This material is chosen due to its durability (Budianto et al., 2022).

Gas Concentration Experiment Set-Up
Propanol solution (absolute, 99.99%) was weighed (mass, \( m \)) inside a sonication device using an analytical balance. The sonication device evaporated the solution and changed it into a gaseous form (Nespeca et al., 2019). This treatment was varied into four different concentrations by varying the evaporation time: \( C_1 \) (30 s), \( C_2 \) (60 s), \( C_3 \) (90 s), and \( C_4 \) (120 s). The evaporated gas was then injected into an exposure chamber (volume \( V = 12 \) L) using a suction pump with a constant flow rate \( (v = 2 \text{ ms}^{-1}) \) (Figure 1) (Budianto et al., 2021). The gas concentration is obtained by dividing the weighed mass by the chamber volume:

\[
C_m = \frac{m}{V} \tag{1}
\]

![Figure 1 Schematic of propanol gas concentration measurement](image)

Performance Test Analysis

The sensitivity \( (S) \) of the developed device is investigated by calculating the calculated gas concentration using a Sauerbrey equation.

\[
\Delta f = - \frac{2 \Delta m f_0^2}{A \sqrt{\rho \mu}} \tag{2}
\]

From the equation above, \( f_0 \) refers to the resonance frequency of the crystal without mass loading (5 MHz). \( A \) is the sensing area (1.256 x \( 10^{-5} \) m), \( \mu \) is the shear modulus of the crystal (2.947 \( \times \) \( 10^{11} \) g.cm\(^{-1} \).s\(^{-2} \)), \( \rho \) is the crystal density (2.643 g.cm\(^{-3} \)) (Budianto et al., 2021; Sauerbrey, 1959).

\[
S = \frac{\Delta f}{C_m} \tag{3}
\]

\[
C_c = \frac{\Delta m}{V} \tag{4}
\]

All data were interpreted as the mean±standard deviation. All treatments were conducted three times to obtain better results. The linearity was investigated by plotting the measured concentration and the calculated one in a linear function approach indicated by an \( R^2 \) value.

3. RESULTS AND DISCUSSION

Propanol Gas Concentration
Measured propanol gas concentrations are interpreted in Table 1. According to this table, the aeration duration influences the measured concentration of \( C_m \). For the mass and measured concentration, the slowest duration (120 s) has 1,214 mg and 101 mg.L\(^{-1}\) of propanol gas, respectively. With a constant volume (12 L), the fastest duration (30 s) has 73 mg.L\(^{-1}\) of propanol gas. This concentration is 28 ppm slower than the 4\(^{th}\) dose. A similar treatment, including chamber volume, gas flow rate, and solution volume, shows that a longer aeration duration generates more propanol gas concentration.

<table>
<thead>
<tr>
<th>Do se ( (n) )</th>
<th>Aerati on Time ( (s) )</th>
<th>( m ) (mg)</th>
<th>( V ) (L)</th>
<th>( C_m ) (mg.L(^{-1}))</th>
<th>( C_c ) (mg.L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>870.0±0.2</td>
<td>1</td>
<td>73±13</td>
<td>0.609±0.047</td>
</tr>
</tbody>
</table>
Frequency Response

Data in Table 2 shows the frequency shift of the QCM sensor related to the exposure treatment. The propanol gas exposure indeed decreases the initial frequency $f_0$. The frequency shift is obtained by subtracting the initial frequency from the measured frequency $f$. According to the resulting data, the lowest $\Delta f$ is 363 Hz. This value is found in $C_m4$, as the smallest dose, has a smaller frequency shift, resulting in 326 Hz compared to $C_m2$ (329 Hz). The difference between each aeration duration is 3 Hz to 20 Hz. It can be assumed that a longer aeration duration is referred to as a more frequency shift.

<table>
<thead>
<tr>
<th>Dose (n)</th>
<th>Aeration Time (s)</th>
<th>$m$ (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>326±25</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>329±30</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>343±46</td>
</tr>
<tr>
<td>4</td>
<td>120</td>
<td>363±21</td>
</tr>
</tbody>
</table>

Sensor Performance

According to the Sauerbrey equation (Eq. (2)), the sensor can measure propanol gas concentration by measuring $\Delta f$ and calculating the deposited mass ($\Delta m$). In line with this, Figure 2 compares measured and calculated propanol gas concentrations. This comparison is interpreted as a linear regression, indicated by $R^2$ > 0.70 ($R^2 = 0.90$). This coefficient shows that the calculated concentration is linearly correlated with the comparator value (measured propanol gas concentration). It shows that the highest concentration is $C_{c4}$, 0.678 µg.L$^{-1}$. In contrast, the smallest concentration is 0.609 µg.L$^{-1}$ ($C_{c1}$).

![Figure 2](image1.png)

Figure. 2 Comparison between measured and calculated propanol gas concentrations (average±SD)

Sensor performance can be analyzed by calculating the sensitivity level ($S$) from varying the propanol gas concentration. Figure 3 shows that the sensitivity decreases when the concentration increases. According to the trendline approach, the data have a regression coefficient ($R^2$) of 0.89 with a correlation coefficient ($r$) of 0.94. This regression analysis shows that the maximum sensitivity is the 1st dose, 5 Hz.L.mg$^{-1}$. Meanwhile, the lowest sensitivity is obtained from the 4th dose, 4 Hz.L.mg$^{-1}$.

![Figure 3](image2.png)

Figure. 3 The sensitivity level of the tested between measured and calculated propanol gas concentrations

According to the accuracy calculation, the system accuracy is below 1%. As expected, this accuracy is in line with the estimation or prediction. In this case, a bare QCM sensor can sense propanol gas with a small concentration. There is a significant difference between the measured and calculated gas concentrations. This performance is caused by the bare QCM characteristic related to the absence of sensitive
coating film. These results also suggest that bare QCM is only a gravimetric crystal that has the potential to be used as a sensor when coated by a specific film (Budianto et al., 2022; Sakti et al., 2019). As a gravimetric sensor, a bare QCM sensor can detect a gas because of the mass change caused by the adsorption and desorption of gas molecules on its surface. This interaction causes a change in the resonant frequency of the QCM (Kang et al., 2021). The detection mechanism of the QCM sensor is based on the relationship between the decrease in frequency and the increase in mass caused by mass loading deposited on the surface of the piezoelectric crystal. The relationship is explained through the Sauerbrey equation (Sauerbrey, 1959). QCM is determined as a mass-type sensor because of its simplicity as a gravimetry-based detection system and low cost. The sensitivity and selectivity of the QCM sensor can be increased by developing the right sensor material to detect certain gases (Wang et al., 2017).

4. CONCLUSION

A propanol concentration measurement device has been developed based on silver electrodes quartz crystal microbalance (QCM). The concentration of propanol gas is linearly correlated to the frequency shift resulting in the QCM with the regression coefficient of ($R^2 > 0.75$). The device can measure propanol gas concentrations $< 1$ Hz.L.$\mu$g$^{-1}$ with a 5 Hz/ppm sensitivity.

6. REFERENCES


Mokoena, Teboho P. Hillie, Kenneth, T. H.,...


