Chitosan-Based Quartz Crystal Microbalance for Alcohol Sensing

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Abstract: Short-chain alcohols are a group of volatile organic compounds (VOCs) that are often found in workplaces and laboratories, as well as medical, pharmaceutical, and food industries. Real-time monitoring of alcohol vapors is essential because exposure to alcohol vapors with concentrations of 0.15–0.30 mg·L⁻¹ may be harmful to human health. This study aims to improve the detection capabilities of quartz crystal microbalance (QCM)-based sensors for the analysis of alcohol vapors. The active layer of chitosan was immobilized onto the QCM substrate through a self-assembled monolayer of L-cysteine using glutaraldehyde as a cross-linking agent. Before alcohol analysis, the QCM sensing chip was exposed to humidity because water vapor significantly interferes with QCM gas sensing. The prepared QCM sensor chip was tested for the detection of four different alcohols: n-propanol, ethanol, isoa myl alcohol, and n-amyl alcohol. For comparison, a non-alcohol of acetone was also tested. The prepared QCM sensing chip is selective to alcohols because of hydrogen bond formation between the hydroxyl groups of chitosan and the analyte. The highest response was achieved when the QCM sensing chip was exposed to n-amyl alcohol vapor, with a sensitivity of about 4.4 Hz·mg⁻¹·L. Generally, the sensitivity of the QCM sensing chip is dependent on the molecular weight of alcohol. Moreover, the developed QCM sensing chips are stable after 10 days of repeated measurements, with a rapid response time of only 26 s. The QCM sensing chip provides an alternative method to established analytical methods such as gas chromatography for the detection of short-chain alcohol vapors.

Keywords: Quartz crystal microbalances; chitosan; L-cysteine; self-assembled monolayer; alcohol compounds

1. Introduction

Detection of volatile organic compounds (VOCs) such as alcohols, ethers, esters, haloalkanes, ammonia, and NO₂, has gained the interest of researchers across the globe since a few decades ago for environmental protection, human health, industrial processing, and quality control [1]. Volatile alcohols such as methanol, ethanol and propanol are organic compounds often found in workplaces and laboratories, as well as medical, pharmaceutical, and food industries. Long-term exposure to alcohol vapor with a concentration of up to 0.15–0.30 mg·L⁻¹ can cause serious health problems, such as eyesight disturbance, nasal and mucous membrane inflammation, conjunctival inflammation,
respiration disruption, nerve disease, lung irritation, and even death [2]. Thus, the real-time monitoring of the presence of alcohols in the air is required.

Fourier transform infrared spectroscopy, gas chromatography, and mass spectrometry are often used to detect alcohol vapors [3]. Although these standard methods are accurate and reliable, they are not real-time, require expensive instrumentations, and are time-consuming, which make them difficult to apply in different conditions. The development of a low-cost sensing system with high accuracy and sensitivity for the detection of alcohol has drawn significant attention recently.

Several sensing systems have been developed based on the sensing principle of electrical resistance, photoelectricity, optics, and acoustic waves [4]. The quartz crystal microbalance (QCM) is a type of acoustic wave sensor. It provides a highly sensitive, real-time, and low-cost method for vapor detection and is often used for gas/vapor [5–7] and humidity [8,9] detection. The sensitivity and selectivity of the QCM system can be improved by coating the electrode with specific materials, including polymers [9,10], metal oxides [11], and other functional materials [12]. Chitosan is one of the natural polysaccharide polymers containing the hydroxyl (-OH) and amino (-NH₂) groups. Chitosan has many promising properties, such as excellent film-forming capability, high mechanical strength, hydrophilicity, and even antibacterial properties. Therefore, chitosan has been widely used as a gas sensor to detect alcohol vapors and other VOCs [13].

Several methods have been developed to coat the QCM substrate with polymer thin film, including drop casting [14], electrospinning [15,16], and self-assembled monolayer (SAM) methods [17]. A vapor-sensing system fabricated via the SAM method is physically more robust than those fabricated by other methods. Moreover, the SAM method is easy to implement and economical [18]. We used L-cysteine and glutaraldehyde to fabricate the chitosan-based QCM sensors. This study aims to develop an alcohol vapor detector based on the QCM coated with chitosan polymer attached to the surface through a covalent bond. The capability of the QCM-based chitosan sensing system will be illustrated by the frequency shift due to variation in alcohol concentrations. The chitosan-based QCM sensing systems are tested for the detection of four different alcohols that are n-amyl alcohol, isoamyl alcohol, n-propanol, and ethanol. For comparison, a non-alcohol of acetone was also tested. A calibrated measurement system, including the frequency counter of QCM used in this study, was build using a standard Pierce-gate oscillator and microcontroller.

2. Materials and Method

Chitosan with medium molecular weight \((M_W = 190,000 \text{ to } 310,000 \text{ g·L}^{-1})\), L-cysteine (HSCH₂CH(NH₂)CO₂H, CAS#52-90-4), glutaraldehyde (GA) (50%), n-amyl alcohol, isoamyl alcohol, n-propanol, and ethanol were purchased from Sigma-Aldrich, St. Louis, MO, USA. Acetic acid and doubly distilled water were purchased from Merck, Darmstadt, Germany. The chemicals were used as received without further purification. The 10-MHz resonant frequency of AT-cut QCM chips with Au electrode diameter of 6 mm was purchased from Novaetech, Turin, Italy.

L-cysteine solution of 1% (w/w) was obtained by dissolving 0.1-g L-cysteine powder in distilled water using a magnetic stirrer at 25 °C and diluted using a 10-mL volumetric flask. Glutaraldehyde solution of 5% (w/w) was obtained by dissolving 1 mL of concentrated glutaraldehyde (50% w/w) in distilled water and diluted to the mark with a 10-mL volumetric flask. Chitosan solution was prepared by mixing 0.05-g chitosan powder with 5.05 mL of 1% (w/w) acetic acid and was mechanically stirred at 600 rpm for 3 h at 60 °C.

The QCM sensor chip was prepared by the following steps. The QCM substrate was first immersed in a 1% L-cysteine solution for 24 h. It was rinsed with distilled water and acetone. After air drying, the QCM chip was immersed in a 5% glutaraldehyde solution for 30 min, followed by rinsing with distilled water. In addition, after air drying, the QCM chip was immersed in a 1% chitosan solution for 2 h. The chip was air dried for 24 h in a dry box. Figure 1 displays the layout of the QCM substrate.
Figure 1. Schematic chemical structure and active layer deposition of the chitosan-based QCM chip for alcohol sensing.

The scheme of the static-type alcohol vapor analytical system was described in a previous study [19]. The frequency counter of QCM was built using a standard Pierce-gate oscillator and microcontroller with 32-bit timer/counter resolution and 42 MHz frequency clock. The configuration of the frequency counter uses double edge mode to get a measurement resolution of less than 0.5 Hz. The frequency counter was placed directly on top of the oscillator circuit to avoid interference. The QCM chip was installed in a 1.25-L testing chamber. The temperature and humidity inside the chamber were adjusted to 33 ± 2 °C and 45–55 %, respectively. It was monitored with a calibrated Sensirion SHT31. The measurement system was connected to a PC equipped with LabVIEW software. This measurement system was calibrated using AFG-2125 Function Generator (GW INSTRUMENT Co., Ltd., Taiwan). A 1–10 µL syringe (Model 701 RN SYR, Hamilton Company, Switzerland) was used for analyte injection. The concentration of the injected analyte in the chamber was expressed in mg·L⁻¹ and calculated using density, percent purity, and volume of analytes. Figure 2 shows the experimental setup of the modified QCM system.

Figure 2. Experimental setup of the QCM system for gas or vapor sensing.

3. Results and Discussion

The QCM gold electrode was coated with chitosan via a self-assembly monolayer of L-cysteine. Chitosan was attached to L-cysteine through a coupling agent of glutaraldehyde. After consecutive coating with L-cysteine, glutaraldehyde, and chitosan, the obtained frequency shift of QCM was 176.5 Hz, 571.5 Hz, and 12750.5 Hz, respectively. The decrease in resonant frequency indicates that the active layer has been deposited on top of the QCM electrodes. The progression of the frequency shift
on the chitosan-based QCM sensor could be attributed to successful surface modification by self-assembly monolayer and polymer attachment. The thickness and hydrophilicity of the film deposited on the QCM substrate affect the frequency shift upon contact with different humidities [20,21].

Knowing that the response of the modified QCM sensor is highly dependent on the ambient relative humidity (RH), we also investigated the response of our chitosan-modified QCM sensor to the RH value. By injecting a small amount of distilled water into the chamber, the RH increased from 48% to 54%. The linear correlation between humidity shift and frequency response of the QCM sensor is shown in Figure 3. Please note that the slope is about $-6.58 \text{ Hz/}%\text{RH}$, with a correlation coefficient ($R^2$) of 0.995. The results show the significant effect of the RH on the frequency change. This phenomenon could be attributed to the hydrophilicity of the chitosan.

Figure 3. The resonant frequency shift of chitosan-based QCM alcohol sensor under the influence of different RH values.

After investigating the effect of the relative humidity (RH) on the QCM response, we used it to investigate four different analytes that are n-amyl alcohol, isoamyl alcohol, n-propanol, and ethanol. Figure 4a shows the response of the developed QCM sensor after contacting with alcohol at a concentration of 7 mg·L$^{-1}$. The analyte was injected into the chamber after 50 s when the resonant frequency of the QCM sensor was stable. After injection, the resonant frequency decreased rapidly for a few seconds and reached a steady value after 100 s. The frequency shift after injection was determined to be about 39, 24, 5, and 3 Hz for n-amyl alcohol, isoamyl alcohol, n-propanol, and ethanol, respectively. Figure 4b shows the RH and temperature readings in the gas sensing chamber during measurement. The RH and temperature values changed slightly during measurement, about 0.25% and 0.4°C, respectively. As mentioned previously, the QCM vapor sensor was profoundly influenced by the humidity and temperature changes. Therefore, the RH and temperature were controlled during measurement to minimize their effect on the frequency reading.

Figure 5a shows the response of the developed QCM sensor to different analytes. The analyte with the concentrations of 1–37 mg·L$^{-1}$ was consecutively injected into the chamber after the frequency response reached a steady state. The frequency shift was recorded after 150 s of analyte injection. The slope of the linear fit of frequency shift versus analyte concentration, shown in Figure 5a, shows the sensitivity of the QCM alcohol sensor. The sensitivity is the highest for n-amyl alcohol and the lowest for ethanol. The correlation coefficient ($R^2$) of the proposed QCM sensor for all analytes is 0.999, which indicates good linearity. The QCM sensor also shows good reproducibility, as indicated by its low standard deviation.
Figure 4. (a) Frequency shift of the chitosan-based QCM sensing system after contact with alcohols at 7 mg·L⁻¹ and (b) the drift of RH and temperature of the sensing chamber throughout the measurement.
Figure 5. (a) Frequency shift of the chitosan-based QCM sensing system after being exposed to alcohols with different concentrations (error bar was determined based on standard deviation of 3-times repeated measurement) and (b) calculated sensitivity.

The sensitivity for different alcohols is shown in Figure 5b. The sensitivity increases in the following order: ethanol, n-propanol, isoamyl alcohol, and n-amyl alcohol. This seems to be directly related to the molecular weight of the alcohols. N-amyl alcohol has the highest molecular weight of 88.15 g·mol⁻¹, giving a sensitivity of 4.4 Hz·mg⁻¹·L. Meanwhile, ethanol has the lowest molecular weight of 46.07 g·mol⁻¹, with a sensitivity of 0.4 Hz·mg⁻¹·L. The physical properties of the analytes are listed in Table 1.

| Analytes       | Molecular weight (g·mol⁻¹) | Vapor pressure (mmHg) | Boiling point (°C) | Sensitivity (Hz·mg⁻¹·L) | LOD (mg·L⁻¹) | Time constant/t₉₀ (s) |
|----------------|---------------------------|-----------------------|--------------------|-------------------------|--------------|----------------------|
| n-Amyl alcohol | 88.15                     | 2.20                  | 138                | 4.4                     | 0.25         | 42/91                |
| Isoamyl alcohol| 88.14                     | 2.37                  | 131                | 3.1                     | 0.50         | 28/62                |
| n-Propanol     | 60.09                     | 21                    | 97                 | 0.9                     | 1.22         | 7.2/17               |
| Ethanol        | 46.07                     | 55                    | 78                 | 0.4                     | 2.86         | 6.7/15               |
| Acetone        | 58.08                     | 231                   | 56                 | 0.1                     | 11.43        | 1.6/3.6              |
This shows that the molecular weight of the analyte seems to affect the sensitivity. However, for isomeric alcohol of n-amyl alcohol and isoamyl alcohol, it is not the case. As pointed out in the previous studies [22,23], for isomers of alcohol, the response of the QCM sensor depended on the length of the alcohol chain. The highest sensitivity for n-amyl alcohol could be due to its linear structure (Figure 5b). Another study shows that the hydrogen bond also influenced the sensitivity of isomers of alcohol [24].

The hydrogen bond affects the boiling point of alcohol. The boiling point of n-amyl alcohol is higher than that of isoamyl alcohol (see Table 1). N-amyl alcohol gives a frequency response greater than the branched alcohol of isoamyl alcohol. The steric hindrance causes isoamyl alcohol to interact moderately with chitosan, which results in a smaller frequency response than that of n-amyl alcohol.

The limit of detection (LOD) can be determined based on the standard deviation of blank QCM measurement and the slope of the plot of the frequency shift versus analyte concentration of Figure 5 [25]. The LOD may be expressed as $3.3 \sigma / S$ (mg L$^{-1}$), where $\sigma$ is the standard deviation of the blank air measurement (0.34, 0.47, 0.33, and 0.34 Hz), and $S$ is the slope of the calibration curve (4.4, 3.1, 0.9, and 0.4 Hz·mg$^{-1}$·L) for n-amyl alcohol, isoamyl alcohol, n-propanol, and ethanol, respectively. The calculated LOD of chitosan-based QCM sensing system can be seen in Table 1.

Figure 6 shows the frequency response of the modified QCM sensing system to 7 mg·L$^{-1}$ of n-amyl alcohol vapor. The frequency shift follows the first order and fits to the first-order instrument fitting. The time constant was achieved after 42 s. The time constant ($\tau$) is defined as the time required for an instrument to reach 63.2% of its maximum response value [26]. Moreover, the response value equaling 0.9 of the maximum response ($R_{90}$) was achieved within 90 s, which determined the response time of the device.

![Figure 6. The frequency shift of chitosan-based QCM sensor after being exposed to 7 mg·L$^{-1}$ n-amyl alcohol.](image)

The response time is crucial for gas sensing, particularly in that for rapid detection. In this study, the response times increased in the following order: ethanol, n-propanol, isoamyl alcohol, and n-amyl alcohol. The response time is related well to the different vapor pressures of analytes. The vapor pressure of the analyte is related to the capability of the liquid to evaporate at a given temperature. Analytes with high vapor pressure evaporate readily at room temperature. Therefore, the response time will be short. The vapor pressure and response time of the analytes are shown in Table 1. This shows that the response time decreases with the increase in the vapor pressure.

Figure 7a shows the frequency movement of the prepared QCM sensing system for the first 10 days of measurement. The resonant frequency shift is steady after 10 days of operation. The variation in the resonant frequency could be attributed only to the change in the RH and temperature (Figure 7b) [27].
Figure 7. (a) Long-term resonant frequency shift of blank QCM and chitosan-based QCM sensing system for the first 10 days of measurement, and (b) change in RH and temperature for the first 10 days of measurement.

In the QCM sensing system, the decrease in the resonant frequency is proportional to the mass loading on the surface of the QCM substrate. The mass adsorbed on the QCM substrate can be calculated by use of the Sauerbrey equation [28], as expressed in Equation 1:

$$\Delta f = -\frac{2f_0^2}{A}\sqrt{\rho q \mu q} \Delta m$$

where $\Delta f$ is the resonant frequency change (Hz), $f_0$ is the base resonant frequency (10 MHz), $\Delta m$ is the mass change (g), $A$ is the electrode surface area (in this case 0.283 cm$^2$), $\mu q$ and $\rho q$ are the quartz shear modulus ($2.947 \times 10^{11}$ g cm$^{-1}$ s$^{-2}$) and density of quartz crystal (2.648 g cm$^{-3}$), respectively.

Based on the Sauerbrey equation, for the 10-MHz QCM system, the resonant frequency decreases by 1 Hz for each 1.15 ng additional mass. Therefore, the mass of the compound adsorbed by the QCM membrane could be calculated using the Sauerbrey equation. The analyte mass loading for the prepared QCM sensor chip was estimated to be 45.1, 27.7, 5.7, and 3.4 ng when it was in contact with the vapor of 7 mg L$^{-1}$ of n-amyl alcohol, isoamyl alcohol, n-propanol, and ethanol, respectively.

Figure 8 shows the interaction model between the modified QCM surface and the analyte molecules. The high frequency response of the QCM sensing system after being exposed to alcohol vapor is believed to be due to hydrogen bond formation between the hydroxyl group (-OH) of the alcohol molecules and the -OH group of the chitosan. The frequency shift for n-amyl alcohol is the highest. This could be attributed to the high molecular weight of n-amyl alcohol. Although the sensitivity of the chitosan-based QCM sensor for n-amyl alcohol is the highest, its response time is the longest of all because of its low vapor pressure. N-amyl alcohol and isoamyl alcohol have the
same molecular weight. Please note that the linear n-amyl alcohol interacts with chitosan better than branched isoamyl alcohol.

**Figure 8.** Schematic of the interaction mechanism between alcohol and chitosan layer.

### 4. Conclusions

A new chitosan-based QCM sensing system for vapor analysis of short-chain alcohols has been developed using an active layer of chitosan covalently attached to the self-assembly monolayer of L-cysteine. The QCM sensing system yields reproducible and linear resonant frequency responses for ethanol, n-propanol, isoamyl alcohol, and n-amyl alcohol. The resonant frequency response correlates well with the size of the alcohol molecules, in which n-amyl alcohol produces the biggest sensitivity of 4.4 Hz·mg⁻¹·L, whereas ethanol produces the smallest sensitivity of 0.4 Hz·mg⁻¹·L. The response time of the proposed sensing system is also affected by the vapor pressure of the analytes. Ethanol has the shortest response time of 15 s, whereas n-amyl alcohol has the longest response time of 91 s. The resonant frequency shift of the chitosan-based QCM sensing system is relatively stable after a test of 10 days of consecutive measurement. The developed system shows good sensitivity, reproducibility, and short response time for the detection of alcohols in the air. The proposed device could be a useful technology for the rapid and in situ analysis of the vapors of short-chain alcohols and could be an alternative to conventional instrumental methods.

**Author Contributions:** K.T. conceived and designed the experiments, calibrated the frequency measurement system, analyzed the data, and wrote the paper. A.S. performed the experiments, wrote the paper. A.R. and S.N.H. analyzed the data and wrote the paper. R.R., and T.J. designed and developed the frequency measurement system and performed the experiments. A.K., I.S., and R.R. analyzed the data and contributed reagent/materials, and wrote the paper.

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