ENHANCED KNOWLEDGE IN SCIENCES AND TECHNOLOGY
e-ISSN: 2773-6385

EKST

Vol. 4 No. 1 (2024) 330-340
https://publisher.uthm.edu.my/periodicals/index.php/ekst

Development of Highly Sensitive Gas Sensor Using Quartz Crystal Microbalance Dipping Method for Gas Vapour Detection

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DOI: https://doi.org/10.30880/ekst.2024.04.01.038

Article Info

Received: 27 December 2023
Accepted: 13 June 2024
Available online: 27 July 2024

Keywords

gas sensor, Quartz Crystal Microbalance, deposition, gas detection, Volatile Organic Compounds

Abstract

Gas sensors play a critical role in environmental monitoring and industrial safety, particularly in detecting hazardous substances such as Volatile Organic Compounds (VOCs). This research focuses on advancing gas sensor technology through the innovative application of the Quartz Crystal Microbalance (QCM) dipping method. Gas sensor performance is optimized by deposition of calix[6]arene and 4-tert-Butylcalix[4]arene onto the QCM surface, allowing for systematic investigation and customization of sensitivity and selectivity, particularly in VOC detection. Experimental evaluations demonstrate that an increase in number of layers chemical deposition onto QCM sensing surface leads to a corresponding decrease in the impedance peak, showcasing the QCM's heightened sensitivity to mass changes. Toluene has greater molecule interaction with QCM sensor as the value of impedance shows the higher compared to ethanol an acetone. Furthermore, sensitivity analysis towards different concentrations of vapours reveals that lower concentrations result in higher impedance peaks, indicating increased sensitivity on impedance value at lower vapor concentrations. The results highlight the sensor's rapid response and customizable nature, offering a promising avenue for reliable gas detection in diverse applications and contributing to the ongoing evolution of gas sensing technologies.

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1. Introduction

Growing population, along with industrial emissions, vehicle exhaust, and open burning is a major source of pollutants that consistently degrade the natural environment. The detrimental impact of environmental pollutants poses a significant threat to human health, leading to respiratory problems, cardiovascular issues, and other health complications [18]. In the dynamic landscape of sensing technologies, gas sensors play a pivotal role in detecting and monitoring various gases, ensuring environmental safety and industrial security [23]. This research is dedicated to the development of an innovative gas sensor, leveraging the QCM dipping method. With a primary focus on its application in vapor gas detection, this research aims to enhance the sensitivity and precision of gas sensors for a wide range of applications. As industries grapple with the imperative of regulatory compliance and safety measures, the customization potential of QCM-based gas sensors emerges as a transformative solution, advancing the accuracy and responsiveness required in the realm of gas detection.

1.1 Gas Sensor

Gas sensors have witnessed a remarkable evolution, transforming from rudimentary chemical detectors to sophisticated electronic devices that are pivotal in addressing contemporary environmental and safety challenges [35]. Indeed, gas sensors play a crucial role in the environmental system, extending their impact beyond human welfare to encompass the broader ecosystem by monitoring and safeguarding the well-being of various organisms, including plants and animals [5]. As societies worldwide grapple with the consequences of industrialization and urbanization, the need for accurate and efficient gas detection technologies has become more pressing than ever.

Gas sensors offer numerous advantages, deriving from their capability to provide real-time monitoring, high sensitivity, and specificity in detecting various gases. Additionally, these sensors are compact, cost-effective, and versatile, making them well-suited for a broad range of applications, including environmental monitoring, industrial safety, and healthcare [22]. Gas sensors have quick response time and adaptability to various conditions further enhance their effectiveness in ensuring the timely and accurate detection of gases [15]. This proficiency proves vital in mitigating potential hazards and plays a pivotal role in protecting both human health and the surrounding environment.

1.2 Quartz Crystal Microbalance (QCM) as a Sensor

QCM is a highly sensitive and versatile sensor widely utilized across diverse fields, from material science to environmental monitoring [21]. QCM operational foundation lies in the exploitation of the piezoelectric effect intrinsic to quartz crystals, enabling precise measurements of mass changes at an astonishingly minute level on the order of Nano grams [2]. QCM stands at the forefront of sensing technology, utilizing the piezoelectric properties of a precisely cut quartz crystal to detect subtle changes in mass and evident in applications such as ultra-sensitive gas sensing, real-time chemical monitoring, and bio sensing for bio molecular interactions [1] [27]. This brief introduction highlights the QCM's instrumental role across diverse fields, offering precision and sensitivity in translating molecular interactions into measurable data.

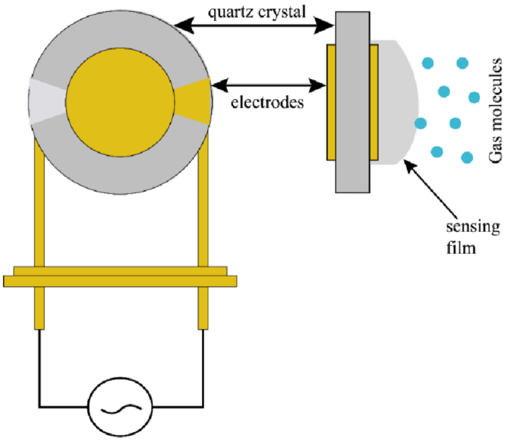


Fig. 1 *Schematic Diagram of QCM Sensor*

As shown in Fig. 1, QCM sensor operates by inducing mechanical oscillations in a precisely cut quartz crystal through the application of alternating current via thin metal electrodes. A sensing film, often deposited on the crystal's surface, interacts with target gas molecules, leading to changes in mass as gas molecules adsorb or desorb on the sensing film, the mass variations on the crystal alter its resonance frequency [11]. The power supply provides the necessary energy for these oscillations. QCM sensor can sensitively and precisely measure the concentrations of gas molecules, showcasing its efficacy in real-time monitoring and detection applications [4].

1.3 Sauerbrey Equation

Sauerbrey equation was established by Ernst Sauerbrey in 1959, which remains the foundation of QCM technology and describes how a quartz crystal resonator’s frequency (Δf) influences its surface mass (Δm) [32]. The equation of Sauerbrey given by:

$$\Delta f = -\frac{2f_0}{n}\Delta m \tag{1}$$

where, Δf defines frequency change, f_0 is the quartz crystal's fundamental resonant frequency, n is the overtone number (1 for the fundamental frequency, 3 for the third harmonic, etc.), and Δm represents mass change [25]. The negative sign indicates that as mass increases, frequency decreases, and vice versa.

The Sauerbrey equation is based on the theory that the resonance frequency of a quartz crystal is inversely proportional to the mass put onto its surface [21]. However, it makes critical assumptions, such as the mass change being minimal in comparison to the baseline mass and the new mass being evenly distributed throughout the crystal surface. While the Sauerbrey equation is an effective tool for analysing mass changes in thin, rigid films, its relevance is limited when dealing with thicker films or elastic substances [28].

In QCM applications, the Sauerbrey equation provides a foundation for analysing processes requiring minute mass changes, such as thin film deposition, molecule binding, and biosensing [3]. Its simplicity and clarity make it a key component of the analytical arsenal, establishing the framework for the development of more complex models to accommodate a wide range of material attributes and experimental situations.

1.4 Chemical Compounds Characterization

1.4.1 Calix[6]arene

Calix[6]arene is a macrocyclic molecular structure of the calixarene family that is produced from phenols and formaldehyde as shown in Fig. 2 [12]. Based on Fig. 2, its name refers to its chalice-like structure, which consists of six phenolic rings joined by methylene bridges. This cyclic configuration gives calix[6]arene unique properties, making it a useful chemical in a variety of applications while the phenolic rings include hydroxyl groups enable a variety of chemical processes and functionalization [12].

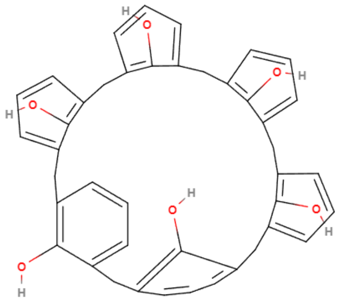


Fig. 2 *2D Calix[6]arene chemical compound structure*

Calix[6]arene's cup-like structure as shown in Fig. 3, which has a hydrophobic interior, makes it easier to recognize and characterize other molecules within its cavity and this characteristic is very useful in host-guest chemistry and supramolecular applications [33]. Calix[6]arene has selective interaction with certain guest molecules, making it useful in molecular recognition, catalysis, and drug administration [6]. Synthetic changes to the phenolic rings or bridge groups enable for adapting the characteristics of calix[6]arene to specific applications, altering aspects such as solubility, reactivity, and host-guest interactions [29]. Thus calix[6]arene is employed in QCM sensors due to its unique structure, which enables selective binding with target molecules, leading to changes in mass that can be detected with high sensitivity, making it valuable for applications in environmental monitoring and medical diagnostics [8][24].

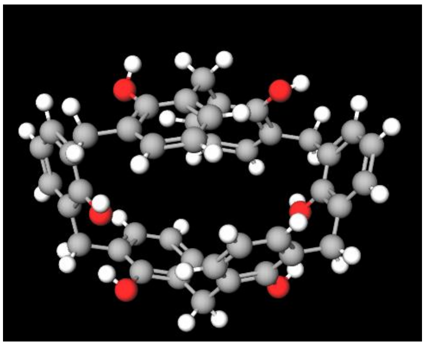


Fig. 3 *3D Calix[6]arene chemical compound structure*

1.4.2 4-tert-Butylcalix[4]arene

4-tert-Butylcalix[4]arene is structure that have phenolic rings as in fig. 4 which has a combination with tert-butyl substituents, which contribute steric hindrance and influence the compound's chemical and physical characteristics [20].

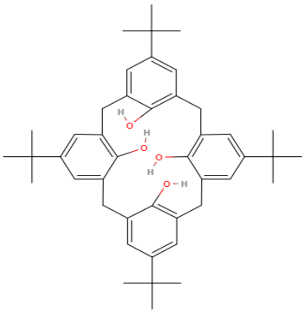


Fig. 4 *2D 4–tert-Butylcalix[4]arene chemical compound structure*

4-tert-Butylcalix[4]arene known as macrocyclic molecule with a characteristic basket-shaped structure made up of four phenolic rings joined by methylene bridges as shown in Fig. 5 [34]. The presence of tert-butyl groups adds steric effects, which influence the accessibility of the hydrophobic cavity produced inside the molecule, therefore, this hydrophobic interior enables 4-tert-Butylcalix[4]arene to preferentially interact with and bind hydrophobic guest molecules [20].

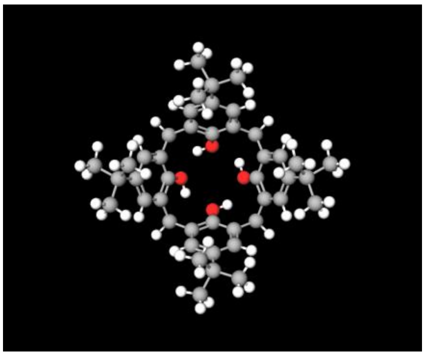


Fig. 5 *3D 4–tert-Butylcalix[4]arene chemical compound structure*

The compound's distinct structure, impacted by both the cyclic organization and the tert-butyl substitutions, makes it ideal for use in supramolecular chemistry, notably host-guest interactions and molecular recognition investigations [17]. The steric hindrance caused by tert-butyl groups influences the compound's reactivity and capacity to establish particular interactions with other molecules, making it an important member of the calixarene class [14]. Therefore, the basket-shaped structure, hydrophobic cavity, and steric hindrance introduced by tert-butyl substituents in 4-tert-Butylcalix[4]arene make it an appropriate sensor deposition method for QCM sensors, improving specificity, sensitivity, and stability in the detection of target analytes.

1.5 Volatile Organic Compounds (VOCs) Detection

VOCs can be harmful to human health and the environment. VOCs, which readily evaporate into the air because its comes from organic chemical group and its characterized as high vapor pressure and less in solubility of water [9] [13]. Some of VOCs, like benzene, are highly toxic and carcinogenic, posing risks to human health and ecosystems, while sick building syndrome highlights health issues arising from prolonged indoor exposure to pollutants [19].

VOCs detection is efficiently achieved using QCM sensors, leveraging their precision in monitoring resonance frequency changes upon interaction with VOCs on the crystal surface [30]. In the realm of VOCs detection, the developed portable interface proves to be a cost-effective, swift, and efficient alternative for utilizing the QCM sensor platform [7]. QCM sensors, coated with crystalline metal-organic framework (MOF) thin films, are employed for the detection of VOCs, enhancing sensitivity and specificity in environmental monitoring and industrial safety applications [36,37]. The QCM sensor, known for its reliability in VOCs detection and versatile in various scenarios, making it a valuable tool applicable in environmental monitoring, industrial safety, and the detection of various substances beyond VOCs.

2. Materials and Methods

2.1 Materials

Calix[6]arene ($C_{42}H_{36}O_6$, 97%) and 4-tert-Butylcalix[4]arene ($C_{44}H_{56}O_4$, 95%) were purchased from Sigma-Aldrich (M) Sdn. Bhd. All chemicals e.g., chloroform, toluene, acetone from QREC (ASIA) Sdn. Bhd. and ethanol from Progressive Scientific Sdn. Bhd. is absolute for research analysis. The Agilent 4294A Precision Impedance Analyzer is the main instrument used in this research. 10Mhz QCM with diameter of 4mm were purchased from Euro Quartz United Kingdom and QCM used in this research as a sensor.

2.2 Methods

QCM was prepared and cleaned with diluted hydrochloric acid (HCL) and rinsed with deionized (DI) water then it dries in ambient air before the experiment. The QCM surface underwent an initial coating with a deposition of calix[6]arene at a concentration of 1 mg ml^{-1}. QCM undergoes dipping method in the chemical solution for 1 minutes 30 seconds and subsequent drying to make sure the chemical solution deposit onto QCM with same condition to produce uniformity. This process was then repeated using 1 mg ml^{-1} solution of 4-tert-Butylcalix[4]arene. The QCM sample that was deposit with two chemicals, calix[6]arene and 4-tert-Butylcalix[4]arene is defined as one pair layers. The experiment then proceeds to two pairs and three pairs of layers to fabricate QCM. The procedure to produce one pair of layers are repeated twice to get two pair of layers as well as to produce three pair of layers which required three times of deposition process for one pair. Subsequently, deposited QCM sensor underwent analysis using an impedance analyser to assess alterations in frequency and impedance.

QCM sensor then exposed to vapours of selected VOCs, namely acetone, ethanol, and toluene in closed container. The VOCs solution is added into the closed container without contact with QCM sensor since it need to detect vapour only as shown in Fig. 6.

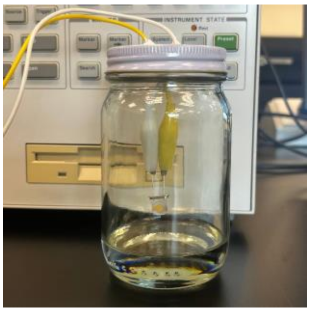


Fig. 6 *QCM sensor testing in closed container*

The gas vapor detection was subsequently analysed using the Agilent 4294A Precision Impedance Analyzer to observe variations in results before and after exposure to vapours. QCM sensors were placed inside a closed container for exposure to VOCs vapour to ensures a controlled environment, allowing precise measurement of the impact of VOCs on QCM impedance. This step aimed to capture any variations in the impedance curves resulting from exposure to different VOCs.

To evaluate the sensitivity of the QCM sensor to different concentrations of VOC vapors (acetone, ethanol, and toluene), the experiment was repeated with dilutions at ratios of 1:100, 1:200, and 1:300. VOCs solution were prepared for detection on QCM sensor according to different ratio as stated in table 1.

Table 1 *Ratios and the calculation*

Ratios	Calculation
1:100	1 ml VOCs chemical (Ethanol/ Acetone/ Toluene) + 100 ml DI water
1:200	1 ml VOCs chemical (Ethanol/ Acetone/ Toluene) + 200 ml DI water
1:300	1 ml VOCs chemical (Ethanol/ Acetone/ Toluene) + 300 ml DI water

1 ml of 100% Ethanol was precisely diluted with 100 ml of deionized (DI) water for the 1:100 ratios. Similarly, 1 ml of Ethanol was mixed with 200 ml of deionized (DI) water for the 1:200 ratios, and 1 ml of Ethanol was mixed with 300 ml of deionized (DI) water for the 1:300 ratios. These dilutions were carried out to evaluate the QCM sensor's performance at various concentration levels. All step is repeated for Acetone and Toluene with same procedure. Therefore, the impedance analyser was employed to analyse variations in results between the original and diluted concentrations of VOCs, demonstrating the sensor's capacity to effectively detect varying concentrations.

Thus, this research main instrument was Agilent 4294A Precision Impedance Analyzer which important to detect impedance change on QCM sensor. Analytical weighing balance also highlighted as it used to weigh chemical compound with the right amount as well as pipette which is used to measure the volume needed for diluting processes.

3. Results and Discussion

3.1 QCM Impedance Analysis

Fig.7 shows a consistent increase in impedance peaks at fundamental frequency, 10MHz was detected in QCM impedance analysis with each resulting pair of layers deposited, showing the cumulative impact of mass loading on the QCM surface. The theoretical mass sensitivity is determined only by the crystal's fundamental resonant frequency and it defined the theoretical mass sensitivity increases proportionally with the fundamental mode [16].

Furthermore, this study showed a correlation between the number of deposited layers and impedance, highlighting the sensor's enhanced sensitivity; fewer layers resulted in higher impedance due to lower mass loading [26]. The results obtained is consistent with predictions and illustrates the complex nature of the QCM sensor's response to variations in mass concentration.

Therefore, the comparison study demonstrated that the impedance peak for one pair of layers was greater than those for two and three pairs, highlighting the effect of concentration on the observed impedance patterns. This sophisticated knowledge expands the use of QCM impedance analysis in researching molecular interactions and gives significant insights for sensor applications and material science applications.

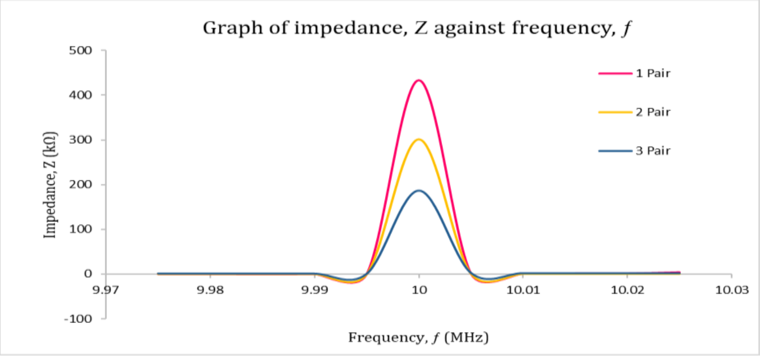


Fig. 7 *The graph of impedance versus frequency for deposition layer by layer in pairing*

3.2 Gas Vapour Detection

During the study, gas vapour detection was focused on three types of VOCs: ethanol, acetone, and toluene. The QCM samples were tested for one pair, two pairs, and three pairs of deposited layers to investigate the effect of layer concentration on gas vapour detection using impedance analyser as shown in fig. 8.

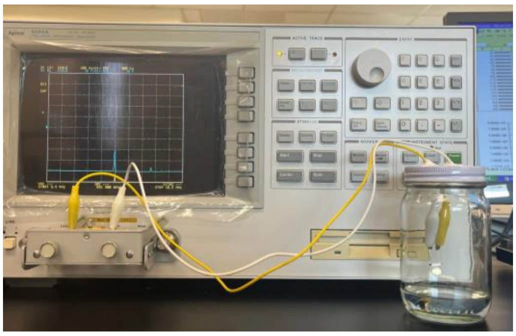


Fig. 8 *Impedance measurement of QCM sensor*

The results in Fig. 9 demonstrated a constant pattern of rising impedance peak, Zp with increasing number of layer pairs. This implies that progressive mass loading on the QCM surface improves its sensitivity, resulting in bigger impedance peaks with a larger number of deposited layers.

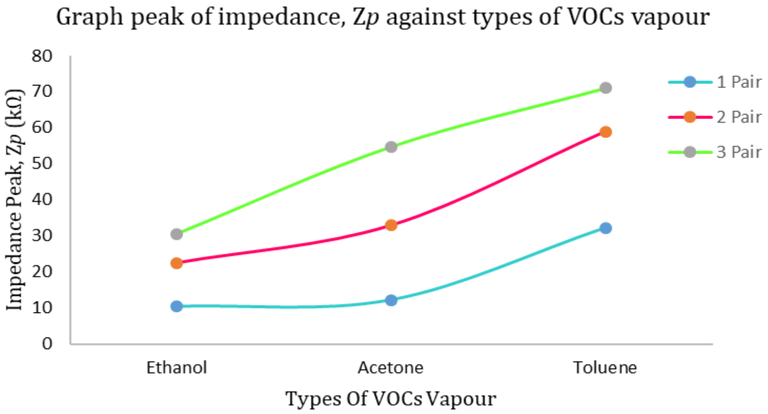
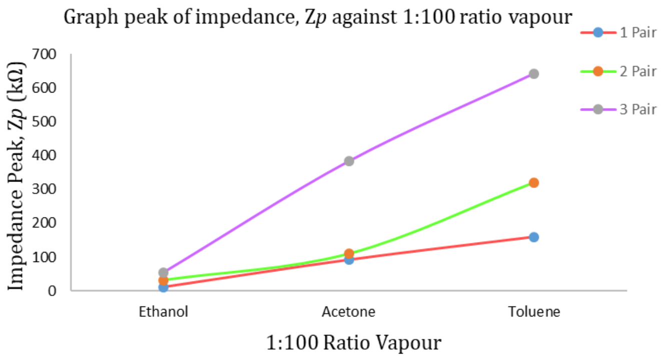


Fig. 9 *The graph of impedance peak versus types of VOCs vapour*

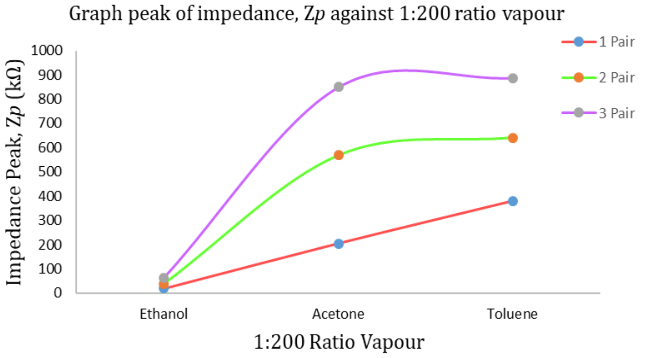
However, when the QCM samples were subjected to Toluene vapour, the measured Zp was much larger than when the samples were exposed to ethanol or acetone vapours. Toluene, which has a larger molecular weight and different chemical properties than ethanol and acetone, is responsible for this unusual reaction [31]. The larger molecular structure of toluene is anticipated to have a greater influence on the QCM surface, resulting in a bigger impedance peak following exposure. From the data, toluene has higher impedance level so the conductivity of toluene is less compared to ethanol and acetone [10]. This finding underscores the selectivity of QCM sensors in detecting different VOCs and highlights Toluene's distinct influence on impedance measurements.

3.3 Sensitivity of QCM Sensor

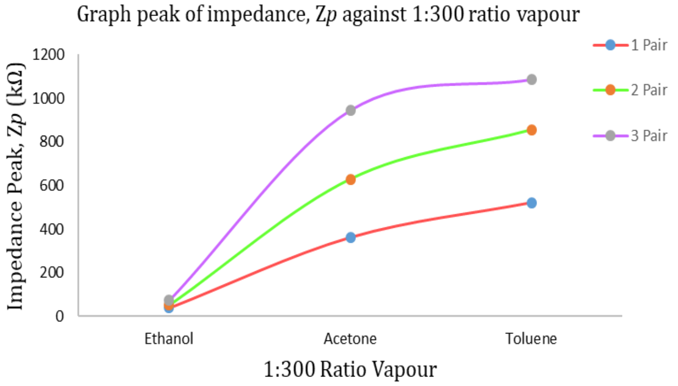
The impedance research conducted with an impedance analyser offered intriguing insights into the sensitivity of the QCM sensor to varied concentrations of VOCs, including Ethanol, Acetone, and Toluene in three different concentration ratios (1:100, 1:200, and 1:300). Fig. 10 shows the graph plotted from impedance peak for each concentration of vapour. The scale on impedance peak in y-axis is different for Fig. 10(a), 10(b) and 10(c). From Fig. 10, the scale on impedance peak in y-axis for 1:100 is smaller than 1:300 and 1:200. This pattern shows the more diluted VOCs vapour, the more the value of impedance. Thus, if the ratio is more than 1:300, the impedance value for each VOCs will increases because the higher the concentration of VOCs, the lower the impedance level.



(a)



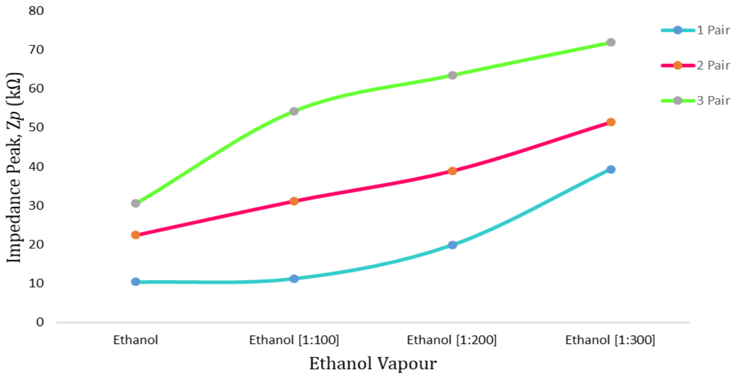
(b)



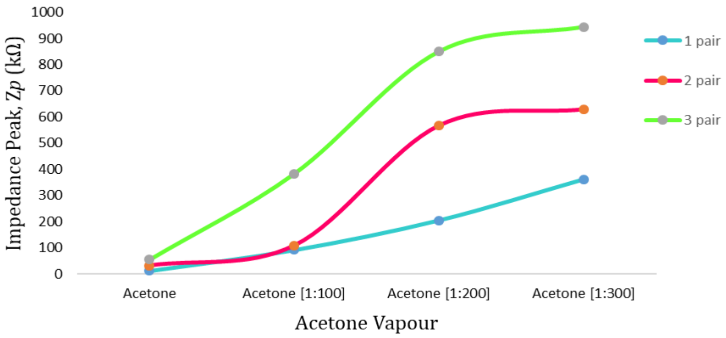
(c)

Fig. 10 *The graph of impedance peak versus ratio concentration of vapours (a) 1:100; (b) 1:200; (c) 1:300*

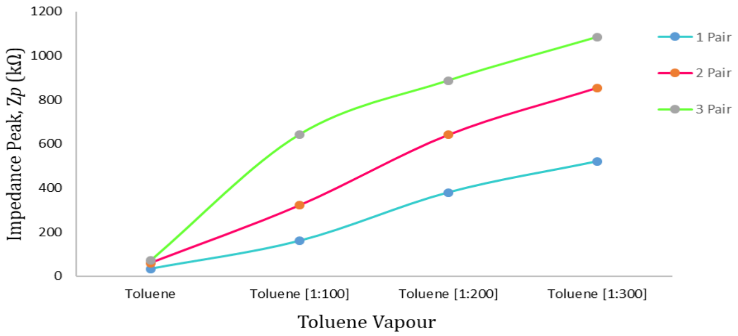
The data collected from the research, as depicted in Fig. 11, highlighted a noteworthy pattern: as the concentration of VOCs decreased, the peak impedance in the impedance analyser increased. This intriguing observation can be attributed to the varying molecular weights and chemical properties of the different VOCs. As the concentration decreases, the mass loading on the QCM surface decreases, allowing for a more pronounced response in terms of impedance. Essentially, the sensor becomes more sensitive to changes in mass at lower concentrations, resulting in higher impedance peaks. This phenomenon underscores the QCM sensor's capability to discern subtle variations in vapor concentration and highlights its sensitivity as a versatile tool for VOC detection.



(a)



(b)



(c)

Fig. 11 *The graph of impedance peak versus types of VOCs vapour (a) Ethanol; (b) Acetone; (c) Toluene*

4. Conclusion

In conclusion, the study of the Quartz Crystal Microbalance Dipping Method for Gas Vapour Detection offered useful insights into the sensitivity and performance of the gas sensor. The research has shown that the QCM sensor displays decreased impedance value as the number of layer deposition chemicals onto QCM increased. As more layers are added, the mass on the QCM surface increases, resulting in lower impedance peak. The impedance graph reveals that Toluene consistently exhibits higher impedance values compared to ethanol and acetone. Toluene, with its heavier aromatic ring, exhibits stronger interactions, leading to lower impedance values. Furthermore, the results on ratio of vapour 1:300 has higher impedance level compared to 1:200 and 1:100. It proves that when concentration of VOCs is less, the impedance value of QCM sensor that exposed to the vapours is higher. The change in resonance frequency and impedance value is directly proportional to the mass change on the crystal surface. Consequently, lower concentrations of VOCs result in a smaller mass change, translating to a higher impedance value in the sensor's response. Furthermore, the sensor's greater sensitivity at lower concentrations increases its usefulness in gas sensing applications. Overall, this study advances very sensitive gas sensors by emphasizing the potential of deposition calix[6]arene and 4-tert-Butylcalix[4]arene onto QCM sensor to achieve successful gas vapour detection in a variety of situations.

Acknowledgement

This was supported by Universiti Tun Hussein Onn Malaysia (UTHM) from the beginning until the research was completed. The authors would like to thank the Faculty of Appplied Sciences and Technology (FAST), Universiti Tun Hussein Onn Malaysia (UTHM) for the support.

Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design, data collection, methodology, analysis and interpretation of results:*** *Nur Firzanah Rosnan and Mohd Kamarulzaki Mustafa. All authors reviewed the results and approved the final version of the manuscript.*

References

[1] Akgönüllü, S., Özgür, E., & Denizli, A. (2022). Recent Advances in Quartz Crystal Microbalance Biosensors Based on the Molecular Imprinting Technique for Disease-Related Biomarkers. *Chemosensors*, *10*(3).

[2] Biologic. (2023). *QCM : History and principles*.

[3] Bruckenstein, S., & Shay, M. (1985). Experimental aspects of use of the quartz crystal microbalance in solution. *Electrochimica Acta*, *30*(10), 1295–1300.

[4] Buckner, C. A., Lafrenie, R. M., Dénommée, J. A., Caswell, J. M., & Want, D. A. (2018). Complementary and alternative medicine use in patients before and after a cancer diagnosis. *Current Oncology*, *25*(4), e275–e281.

[5] Chu, E. W., & Karr, J. R. (2017). Environmental Impact: Concept, Consequences, Measurement ☆. *Reference Module in Life Sciences*, 1–22.

[6] Coquière, D., De La Lande, A., Martí, S., Parisel, O., Prangé, T., & Reinaud, O. (2009). Multipoint molecular recognition within a calix[6]arene funnel complex. *Proceedings of the National Academy of Sciences of the United States of America*, *106*(26), 10449–10454.

[7] Debabhuti, N., Mukherjee, S., Sharma, P., Tudu, B., Bhattacharyya, N., & Bandyopadhyay, R. (2022). Development of a portable gas sensing platform with QCM sensors for volatiles of agro products. *Journal of Materials NanoScience*, *9*(2), 115–119.

[8] Edwards, N. Y., Schnable, D. M., Gearba-dolocan, I. R., & Strubhar, J. L. (2021). *sensors*.

[9] EPA, U. (2022). What are volatile organic compounds (VOCs)? | US EPA. *United States Environmental Protection Agency*, 1.

[10] ESIG. (2013). Flammability - A safety guide for users: Safe working with industrial solvents. *European Solvents Industry Group*.

[11] Evardsson, M. (2020). *Overview Piezoelectricity and the QCM working principle - Biolin Scientific AB*.

[12] Guérineau, V., Rollet, M., Viel, S., Lepoittevin, B., Costa, L., Saint-Aguet, P., Laurent, R., Roger, P., Gigmes, D., Martini, C., & Huc, V. (2019). The synthesis and characterization of giant Calixarenes. *Nature Communications*, *10*(1), 1–14.

[13] Khan, A. A., Bahadar, A., Hussain, M., Ullah, F., Ullah, A., & Rasheed, S. (2023). Analytical evaluation of polymeric CNTs/CuO nanocomposite electrode for the room temperature detection of volatile organic compounds (VOCs). *Results in Chemistry*, *5*(February), 100928.

[14] Lo, P. K., & Wong, M. S. (2008). Extended calix[4]arene-based receptors for molecular recognition and sensing. *Sensors*, *8*(9), 5313–5335.

[15] Ma, M., Yang, X., Ying, X., Shi, C., Jia, Z., & Jia, B. (2023). Applications of Gas Sensing in Food Quality Detection: A Review. *Foods*, *12*(21).

[16] Malin Edvardsson. (2021). *How to read a QCM specification Parameters to keep an eye on , what they mean and why they are important*.

[17] Malinska, M. (2021). Temperature- And solvent-induced crystal-form transformations of the pyridine@p-tert-butylcalix[6]arene host-guest system. *Crystal Growth and Design*, *21*(2), 1103–1112.

[18] Manisalidis, I., Stavropoulou, E., Stavropoulos, A., & Bezirtzoglou, E. (2020). Environmental and Health Impacts of Air Pollution: A Review. *Frontiers in Public Health*, *8*(February), 1–13.

[19] Mirzaei, A., Leonardi, S. G., & Neri, G. (2016). Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: A review. *Ceramics International*, *42*(14), 15119–15141.

[20] Moris, S., Galdámez, A., Jara, P., & Saitz-Barria, C. (2016). Synthesis of novel p-tert-butylcalix[4]arene derivative: Structural characterization of a methanol inclusion compound. *Crystals*, *6*(9).

[21] NanoScience. (2012). *What is a Quartz Crystal Microbalance - QCM What is a Quartz Crystal Microbalance - QCM*.

[22] Naz, S., Javid, I., Konwar, S., Singh, P. K., Sahni, M., & Bhattacharya, B. (2020). Solid state gas sensor. *Materials Today: Proceedings*, *49*, 3245–3249.

[23] Nikolic, M. V., Milovanovic, V., Vasiljevic, Z. Z., & Stamenkovic, Z. (2020). Semiconductor gas sensors: Materials, technology, design, and application. *Sensors (Switzerland)*, *20*(22), 1–31.

[24] Quaglio, D., Polli, F., Del Plato, C., Cianfoni, G., Tortora, C., Mazzei, F., Botta, B., Calcaterra, A., & Ghirga, F. (2021). Calixarene: a versatile scaffold for the development of highly sensitive biosensors. *Supramolecular Chemistry*, *33*(7), 345–369.

[25] Sauerbrey, G. (1959). Sauerbrey equation. *Zeitschrift Für Physik*, *155*, 206–222.

[26] SinePhase. (n.d.). *Shift of resonant frequency in biological piezoelectric sensors.* 2.

[27] Sorption, P., & Polymers, I. (1993). *DEVELOPMENT OF A PIEZOELECTRIC QUARTZ CRYSTAL MICROBALANCE FOR THE MEASUREMENT OF By SHAILESH DESHP ANDE*.

[28] Standford Research Systems. (2004). Quartz Crystal Microbalance Theory and Calibration The QCM oscillator. *Technical Reports*, *408*(408), 744–9040.

[29] Tauran, Y. (2015). *Calix [n] arenes in nano bio-systems Yannick Tauran To cite this version : HAL Id : tel-01127416*.

[30] Temel, F., & Tabakci, M. (2016). Calix[4]arene coated QCM sensors for detection of VOC emissions: Methylene chloride sensing studies. *Talanta*, *153*, 221–227.

[31] Trioni, M. I., Cargnoni, F., Americo, S., Pargoletti, E., Chiarello, G. L., & Cappelletti, G. (2022). Acetone and Toluene Gas Sensing by WO3: Focusing on the Selectivity from First Principle Calculations. *Nanomaterials*, *12*(15), 1–12.

[32] Vashist, S. K., & Vashist, P. (2011). Recent advances in quartz crystal microbalance-based sensors. *Journal of Sensors*, *2011*.

[33] Wang, C., Xu, L., Jia, Z., & Loh, T.-P. (2023). Recent applications of macrocycles in supramolecular catalysis. *Chinese Chemical Letters*, 109075.

[34] Widanelage, L., & Priyadarshana, V. (2019). *Developing a Basket-Shaped Host Molecule Based on P-Tert-Butylcalix[4]arene Featuring Urea Groups for Encapsulating Volatile Guest Molecules Lokugama*.

[35] Wolken, J. C. (n.d.). *The Evolution and Challenges of the Trust Industry*.

[36] Yamagiwa, H., Sato, S., Fukawa, T., Ikehara, T., Maeda, R., Mihara, T., & Kimura, M. (2014). Detection of volatile organic compounds by weight-detectable sensors coated with metal-organic frameworks. *Scientific Reports*, *4*, 1–6.

[37] Abdullah, T. D. N. (2022). Effect of Pectin Coating Enriched with Oregano Essential Oil on the Fresh-Cut Papaya Quality. *Enhanced Knowledge in Sciences and Technology*, *2*(1), 069-078.