Study the Sensitivity of Quartz Crystal Microbalance (QCM) Sensor Coated with Different Thickness of Polyaniline for Determination Vapors of Ether, Chloroform, Carbon tetrachloride and Ethyl acetate

Mohammed Hadi Shinen[1*] Fadhel Omran Essa[1] Atheer Saieb Naji[2]

1- Department of General Science, College of Basic Education, University of Babylon, PO box 4 Iraq
2- Environmental Pollution Department, College of Environmental Sciences, Al-Qasim Green University

* E-mail of the corresponding author: mohammed.shinen@yahoo.com

Abstract

A quartz crystal microbalance (QCM) sensor coated with a thin film of polyaniline was used as a sensitive method for the determination of a number of following vapours: Ether, Chloroform, Carbon tetrachloride and Ethyl acetate. The detection was based on the absorption of the vapours of these organic compounds into the film by using gas cell chamber. The detection of these vapours can be obtained in part per million (ppm). The work includes the use of polyaniline films with different thickness (55, 82, 102 and 153) nm where thickness of the PANI films was controlled by the spin coating process.

Results show that increasing of sensitivity with increase of the concentration of injected analyte when the PANI-film-coated QCM was exposed to the vapours of ethanol, propanol hexane and benzene. Best sensitivity to ethanol and hexane were obtained with film thicknesses 93nm while in the case of propanol best results were obtained with thickness of 118 and 93 nm. Thickness of 93 and 176 nm gave good sensitivity to benzene.

Keywords: QCM, Polyaniline, Vapors, Sensor, Thickness .

1. Introduction

Since the quartz crystal microbalance (QCM), was first introduced by Sauerbrey in 1959, it has become a largely used instrument for small mass measurements in vacuum, gas, and liquid phase. On the other hand, the quartz crystal microbalance (QCM), which became a largely used instrument during the last decades, can detect up to 10^{-16} kg (Mecea 2005). Many years ago, the chemical sensors have made great advances and have taken root in human life and industry as a feature of modern technology. In recent years, polymers have found an increasing role in sensorics due to their unique characteristics, and a number of new sensors have been developed (Hosseini *et al*. 2005). The monitoring of volatile organic compounds (VOCs) has become a serious task due to regulations in many countries of the world. Gas chromatography and infrared spectroscopy require large quantities of samples and are time consuming. Therefore, alternative methods are required (Matsuguchi & Uno 2006). Amongst various types of sensors, there is a considerable interest in QCM (Price *et al*. 2002). When the surface of a quartz crystal electrode is coated with a sensitive coating, capable of interacting with the environment of interest, it is possible to construct a sensitive sensor to the component under investigation; the selection of sensitive coating is a critical task in the design and performance of chemical QCM sensors (Patel *et al*. 2000). The mass of the film (*m*) can be monitored by measuring the oscillating frequency change (Δf) of a quartz crystal and using Sauerbrey equation (Ayad *et al*. 2008):

$$\Delta f = -\left(\frac{2f_o^2}{\sqrt{\rho_Q \mu_Q}}\right) m \qquad \text{------------------1}$$

Where f_o (*Hz*) is the natural frequency of the quartz crystal, ρ_Q is the quartz density (2.649 g/cm3) and μ_Q is the shear modulus (2.947×10^{10} N/m^2). Polymers are widely used as chemically sensitive coating materials on quartz crystal electrodes and are particularly suitable for detecting VOCs; because of the ability of the polymer to sorb vapour reversibly (Sun & Okada 2001). The chemical structure and physical properties of polymeric coatings and the nature of interaction between polymer coatings and vapour molecules determine the selectivity, sensitivity, signal kinetics and reversibility of the sensors (McGill *et al*. 2000). Conducting polymers such as polyaniline (PANI), polypyrrole, and polythiophene have been widely investigated as effective materials for chemical sensors (Matsuguchi *et al*. 2003). The advantages of conducting polymers compared to inorganic materials used until now are their diversity, their easy synthesis and particularly, their sensitivity at room temperature (Schollhorn *et al*. 1998). Furthermore, conducting polymers have good mechanical properties, which allow a facile fabrication of sensors. As a result, more and more attentions have been paid to the sensors fabricated from conducting polymers, and a lot of related articles were published for example polyaniline was found to be a better choice for gases such as ammonia because of its higher sensitivity, reversible response and shorter response time (Sengupta *et al.* 2011). Wang *et al*. (2006) studied the sensitivity, short-term reproducibility, stability, and response time properties of ZnO nanowires-modified quartz crystal as a gas-detecting sensor. Ayad *et al*. (2008) used quartz crystal microbalance (QCM) sensor, coated with a thin film of polyaniline emeraldine base (EB), as a sensitive method for the determination of a number of aliphatic chlorinated hydrocarbons such as carbon tetrachloride, chloroform, dichloromethane, 1,2-dichloroethane vapours. Polyaniline-modified quartz crystal microbalance (QCM) sensor was obtained through immobilizing the polyaniline film on the silver electrode surface of quartz crystal resonator by an electrochemical method and the sensor was studied for detecting the formic acid gas of different concentrations (Yan *et al.* 2012) and a lot of related articles were published for example polyaniline was found to be a better choice for gases such as ethanol, propanol, hexane and benzene because of its higher sensitivity, reversible response and shorter response time(Hani Mahmood Hussien and Mohammed Hadi Shinen 2013). The aim of the present work was to employ different thickness PANI film coated QCM as a sensor for the following vapours: Ether, Chloroform, Carbon tetrachloride and Ethyl acetate.

2- Synthesis of polyaniline

polyaniline is prepared to take the 6 mmol of aniline in 30 ml of hy

drochloric acid concentration 1 M and placed on electromagnetic stirrer for one hour and then cooled to a temperature of – 5 ^{o}C for two hours. After that another solution is prepared consisting of 6 mmol of ammonium peroxidisulphate and added mechanism 30 ml of hydrochloric acid concentration 1 M and placed on board for a period of one hour . Then two solutions are mixed well gradual for two hours to precipitate urinary polyaniline .. Then added a very small amount of sodium hydroxide concentration 1 Murlara into the mix to precipitate minutes polycarbonate polyaniline . Then the solution is washed with distilled water a number of times and then with ethanol and then dried product for a day by a rarefied drying under pressure when the temperature is freezing after getting urinary polyaniline (Pawa et al (2009).

3- synthesis of thin film

Different thickness of PANI films were deposited on both sides of quartz crystal microbalance (QCM) by using spin- coating model (VTC-100 vacuum spin coating) . PANI films obtained were (55, 82, 102 and 153) nm and thickness measurements were achieved by using ellipsometry. Gas cell chamber (controlled by software) was used to measure the sensitivity of QCM when exposed to different analysts of **Ether**, **Chloroform**, Carbon tetrachloride and **Ethyl acetate**. The QCM was exposed to air after the absorption of each analyte. The backshift of the crystal frequency to its initial value was taken as an indication of full desorption. All measurements were carried out at room temperature. Sensitivity is defined as the ability of a sensor to produce a signal when low concentrations of a target analyte are present. The larger the signal, the more sensitive a sensor is. The sensitivity of a sensing material is defined as the concentration of analyte sorbed onto the sensing material divided by the total concentration of the analyte (Stewart 2011).

4. Result and discussion

Figures 1, 2, 3, and 4 show that increasing of sensitivity with increase of the concentration of injected analyte when the PANI-film-coated QCM was exposed to the vapours of Ether, Chloroform, Carbon tetrachloride and Ethyl acetate. This is expected since when more vapor molecules are provided in the test atmosphere, more molecules would be absorbed into the PANI coating on the QCM. After each addition of vapor concentration, the frequency of the crystal was back shifted to its initial value by drying the electrode using air, which indicates full desorption of vapor from the electrode surface. This behaviour confirms that the sensing interaction between the imine and amine sites of PANI chains coating and vapor is a physical absorption through a dipole/dipole interaction or hydrogen bonding. The presence of hydrogen attached to an electronegative nitrogen in all of the polymers allows for hydrogen bonding (Stewart 2011).

Figure 1 shows increasing of sensitivity with increase of the concentration of injected analyte of Ether. The increase in resistivity of the sensor on exposure to Ether is thought to be caused by an interaction via dipole/dipole moment of Ether molecules and the nitrogen atoms of PANI, leading to the hindrance in conformational rearrangements of the macromolecules that impedes electron delocalization and charge transport through the polymer chain (Choudhury 2009). Best sensitivity was obtained with film thicknesses 82 nm at high and low concentration of Ether. So; it is found that the polymer thickness would affect the sensitivity of the sensor. This can be assigned to the increased active sites of the polymer as the film thickness increases (Mirmohseni & Oladegaragoze 2004). Therefore PANI of 82 nm considered suitable thickness to create active sites and but Ether molecules only physically absorb on the PANI surface. On the other hand it was found that thickness of 102 and153 nm gave low sensitivity at high and low concentration to Ether as shown in figure 1 due to poor physically absorb on the PANI surface . Figure 2 illustrates the effect of PANI film thickness on sensitivity of QCM with increase of the concentration of injected analyte of Chloroform. Also it can be seen that with increase in analyte concentration the sensitivity increases, which could be attributed to the interaction via dipole/dipole moment of Chloroform molecules molecules and the nitrogen atoms of PANI. As shown in figure 2 best results were obtained with thickness of 102 and 82 nm. By comparison figure 1 and 2 it can be seen that QCM, with PANI film of thickness 102 nm, has more sensitivity to Chloroform because more physical absorption take place. This is because low molecular weight alcohols vapors decrease the conductivity of the PANI faster than higher molecular weight alcohols. These results are in agreement with the literature. For example, (Josowicz and Janata (1986) and Bartlett and Chung (1989) and Hani Mahmood Hussien and Mohammed Hadi Shinen (2013)) observed a much slower response for ethanol vapor when compared to methanol vapor. It was interpreted that the electrons in the PANI were much more tightly bound in the presence of the low molecular weight alcohol. Figure 3and 4 demonstrates behavior of QCM towards increase of the concentration of injected analyte of , Carbon tetrachloride and Ethyl acetate respectively which both are non-polar molecular. This would then indicate that polarity is not the only factor in generating a response on the nanosensors (Yang 2010). Elucidation of the exact mechanisms would require extensive research with a variety of substances and possible development of structure activity relationships. Also it can be seen that best sensitivity to Carbon tetrachloride was obtained with PANI film thicknesses 82 nm. Figure 4 shows that thickness of 55 nm and 153 nm gave good sensitivity to Ethyl acetate. It is obvious from figure 3 and 4 that QCM has more sensitivity to Ethyl acetate compare to Carbon tetrachloride.

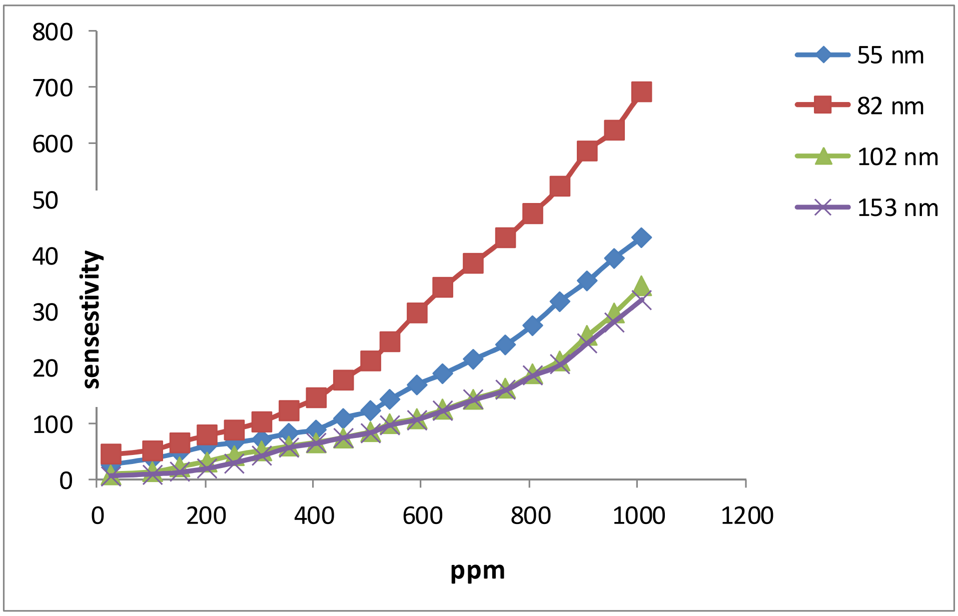

Figure1. Sensitivity of QCM Coated with Different Thickness of PANI Exposed to Ether

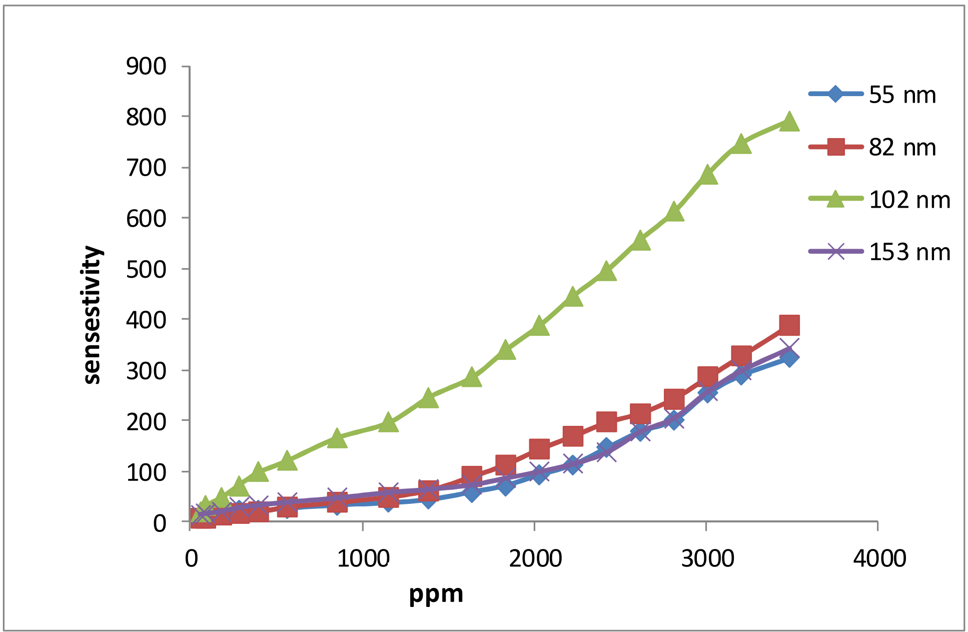

Figure2. Sensitivity of QCM Coated with Different Thickness of PANI Exposed to Chloroform

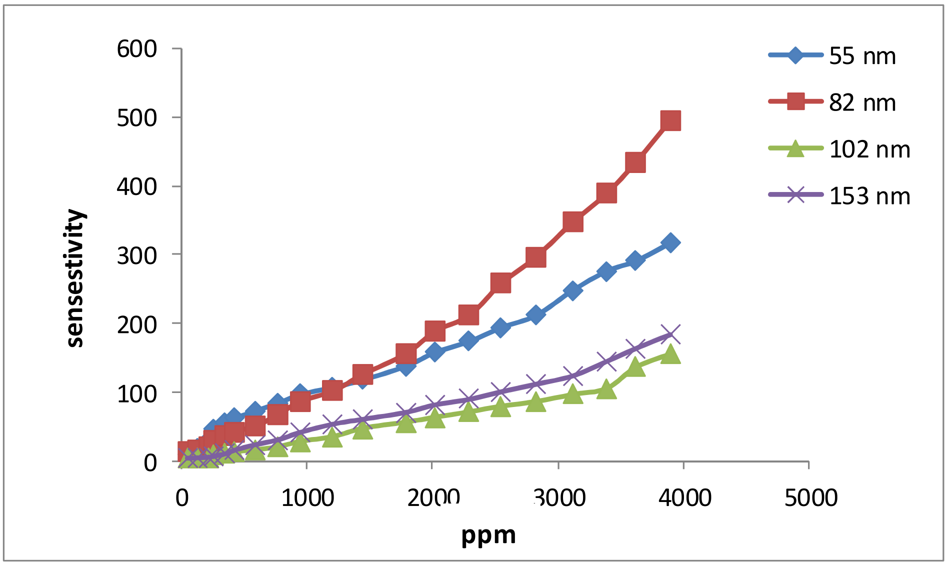

Figure3. Sensitivity of QCM Coated with Different Thickness of PANI Exposed to Carbon tetrachloride

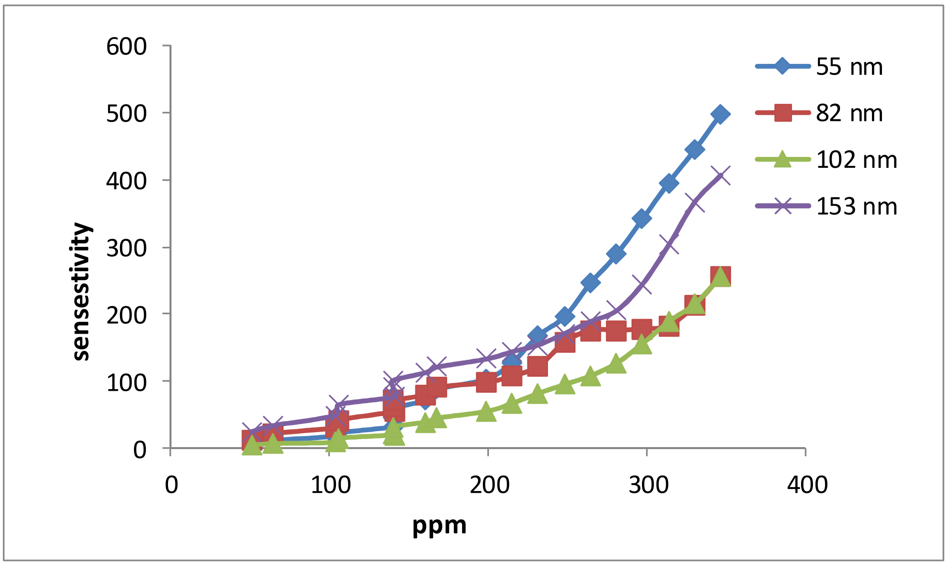

Figure4. Sensitivity of QCM Coated with Different Thickness of PANI Exposed to Ethyl acetate

5. Conclusion

It was found increasing of sensitivity with increase of the concentration of injected analyte when the PANI-film-coated QCM was exposed to the vapours Ether, Chloroform, Carbon tetrachloride and Ethyl acetate. Best sensitivity to Ether was obtained with PANI film thicknesses of 82 nm. Thickness of 55 nm and (102, 153) nm gave low sensitive to Ether due to poor physically absorb on the PANI surface. PANI film thicknesses of 102 nm gave best sensitivity Chloroform. Using thickness of 82 nm and 55 nm gave good sensitivity to Carbon tetrachloride.While best sensitivity to and Ethyl acetate was achieved by using PANI film of thickness 55 nm.

References

Mecea, V.M. (2005), "Mini Review from Quartz Crystal Microbalance to Fundamental Principles of Mass Measurements", *Analytical Letters* 3, 753–767.

Hosseini, S.H., Oskooei, S.H.A. & Entezami, A.A. (2005), "Toxic Gas and Vapour Detection by Polyaniline Gas Sensors", *Iranian Polymer Journal* 14 (4), 333-344.

Matsuguchi, M. & Uno, T. (2006), "Molecular Imprinting Strategy for Solvent Molecules and its Application for QCM-Based VOC Vapour Sensing", *Sens. Actuators B* 113, 94–99.

Price, G.J., Clifton, A.A., Burton, V.J. & Hunter, T.C. (2002), "Piezoelectric Chemical Sensors Based on Morpholine Containing Polymers", *Sens. Actuators B* 84, 208–213.

Patel, R., Zhou, R., Zinszer, K. & Josse, F. (2000), "Real-Time Detection of Organic Compounds in Liquid Environments Using Polymer-Coated Thickness Shear Mode Quartz Resonators", *Anal. Chem.*72, 4888–4898.

Yan, Y., Lu,H., D., Zhou, H.H., Zhang, T., Wu, L. & Cai, L. (2012), "Polyaniline-modified quartz crystal microbalance sensor for detection of formic acid gas", *Water, Air, & Soil Pollution* 223(3), 1275-1280.

S.G.Pawar, S.L.Patil, A.T.Mane, B.T.Raut, V.B.Patil, Archives of Applied Science Research, 2009, 1 (2), 109.]

Ayad, M.M., Hefnawey, G.E. & Torad, N.L. (2008), "Quartz Crystal Microbalance Sensor Coated with Polyaniline Emeraldine Base for Determination of Chlorinated Aliphatic Hydrocarbons", *Sensors and Actuators B* 134, 887–894 .

Sun, L.X. & Okada, T. (2001), "Studies on Interactions between Nafion and Organic Vapours by Quartz Crystal Microbalance", *J. Membr. Sci*. 183, 213–221.

McGill, R.A., Mlsna, T.E., Chung, R., Nguyen, V.K. & Stepnowski, J. (2000), "The Design of Functionalized Silicon Polymers for Chemical Sensor Detection of Nitroaromatic Compounds", *Sens. Actuators B* 65, 5–9.

Stewart, K.M.E. (2011), "Doped Polyaniline for Gas Sensors for the Detection of Formaldehyde", *MSc thesis*, University of Waterloo, Applied Science, Chemical Engineering.

Choudhury, A. (2009), "Polyaniline/Silver Nanocomposites: Dielectric Properties and Ethanol Vapour Sensitivity", *Sensors and Actuators B* 138, 318–325.

Mirmohseni, A. & Oladegaragoze, A. (2004), "Determination of Chlorinated Aliphatic Hydrocarbons in Air Using a Polymer Coated Quartz, Crystal Microbalance Sensor", *Sens. Actuators B* 102, 261–270.

Josowicz, M. & Janata, J. (1986), "Suspended Gate Field-Effect Transistor Modified with Polypyrrole as Alcohol Sensor", *Anal. Chem.* 58, 514–517

Bartlett, P.N. & Chung, L.S.K. (1989), "Conducting Polymer Gas Sensors 3 Results for 4 Different polymers and 5 Different Vapors", *Sens.Actuators B* 20, 287–292.

Yang, C.H. (2010), "Development of Nanosensor to Detect Mercury and Volatile Organic Vapors , *MSc thesis*, Department of Civil and Environmental", Duke University.

Hani Mahmood Hussien and Mohammed Hadi Shinen. (2013), Study the Sensitivity of Quartz Crystal Microbalance (QCM) Sensor Coated with Different Thickness of Polyaniline for Determination Vapours of Ethanol, Propanol, Hexane and Benzene