

## Detection of Nitrobenzene using a coated Quartz Crystal Microbalance with a Parametric Modeling Approach

Dipali Ramdasi<sup>1\*</sup> and Rohini Mudhalwadkar<sup>2</sup>

<sup>1</sup>*Department of Instrumentation and Control, Cummins College of Engineering for Women, Karvenagar, Pune, 411052, India*

<sup>2</sup>*Department of Instrumentation and Control, College of Engineering, Pune, 411005, India*

### ABSTRACT

Nitrobenzene (NB) is a nitroaromatic compound possessing explosive properties. Timely detection of this compound will prevent emotional and financial losses to mankind. As direct sensors are not available, a parametric modeling approach is developed using the coated Quartz Crystal Microbalance (QCM). These sensors are mass sensitive and can measure changes in mass in few micrograms. When the sensing electrode is deposited with a chemically sensitive coating, adsorption of gas molecules occurs at the surface when exposed to a gas. This results in increased deposited mass and decrease in resonant frequency. This increase in mass is proportional to the gas concentration. A parametric model is derived for coated QCM using the Diffusion reaction model and kinetic analysis to estimate the gas concentration. When the concentration is beyond permissible limits, precautionary measures can be taken to prevent heavy losses. The parameters of sensing layer density and thickness, resonant frequency of quartz, exposition time were used to develop the model along with standard crystal parameters. The developed parametric model was validated experimentally using an AT cut 10MHz crystal, deposited with a sensitive coating of Polyaniline, Tungsten Oxide, Palladium and Dimethyl Sulfoxide. The GAMRY Electrochemical Quartz Crystal Microbalance (EQCM) was used for acquiring and analyzing the response of the QCM for NB sensing. The model was validated analytically with the Extended Butterworth Van Dyke (EBVD) model, rearranged for gas concentration determination. The model performed with an accuracy of 74% for concentrations higher than 300 ppb.

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#### E-mail addresses:

[dipali.ramdasi@cumminscollege.in](mailto:dipali.ramdasi@cumminscollege.in) (Dipali Ramdasi)

[rpm.instru@coep.ac.in](mailto:rpm.instru@coep.ac.in) (Rohini Mudhalwadkar)

\* Corresponding author

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## INTRODUCTION

For years, countries like Iraq, Syria, India, Afghanistan and many more have experienced terrorist activities, leading to the death of hundreds of soldiers and innocent people every year. These countries bear a huge monetary loss for dealing with such incidents. According to a recently submitted report (Institute for Economics & Peace, 2018), India ranks 7<sup>th</sup> in the list of countries facing maximum terrorist attacks. The use of nitroaromatic explosives for destructive intentions is observed over the recent years. Thus, there is a need for timely detection of these explosives to avoid mishaps. Nitrobenzene (NB) (PubChem CID 7416) is an organic compound with the chemical formula  $C_6H_5NO_2$ . Mixtures with NB are found to be highly explosive with high sensitivity and detonation velocity as mentioned by Meyer et al. (2016), Giannoukos et al. (2016), Qingsong et al. (2007) and Woodfin (2006). The use of NB as an element of explosive mixtures was reported 50 years ago by Mason et al. (1965). It is a water insoluble pale-yellow oil with almond like odour. This paper deals with detection of NB as a potential explosive using a parametric modeling approach. As direct sensors for NB are not available, this method will result in the refinement of physical measuring techniques. For this, the Quartz Crystal Microbalance coated with a layer sensitive towards NB was used. The coated crystal was then subjected to varying concentrations of NB and the response of the sensor in terms of deviation in resonant frequency was observed. The concentration of NB was then estimated from the developed model substituting the observed sensor response. The basic properties of QCM, thin film sensors and the method adopted for developing the model are further discussed.

## MATERIALS AND METHODS

### Quartz Crystal Resonator

When the Quartz Crystal Resonator (QCR) is deposited with material of a very low mass of a few micrograms, a change in the resonating frequency is observed as stated by Fraden (2015) and Vives (2008). The deposited mass is proportional to change in resonant frequency and can be calculated using the Sauerbrey's equation as proposed in an earlier article (Sauerbrey, 1959).

$$\Delta f = \frac{-2f_0^2 \Delta m}{A\sqrt{\rho_q G_q}} \quad [1]$$

This property of QCR can be used for detecting a Volatile Organic Compound (VOC) if the change in mass is due to a VOC. For this, the QCM is deposited with a polymer based chemically sensitive coating as presented by Reglero et al. (2018), Temel and Tabakci (2016), Bai and Shi (2007), Seena et al. (2011) and Menon et al. (1998) and is shown in Figure 1.

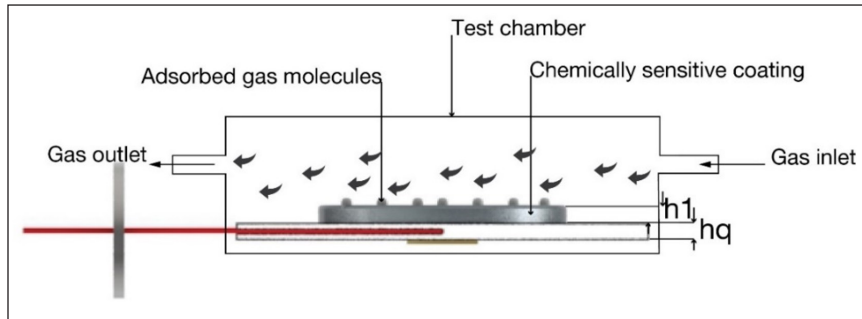


Figure 1. Adsorbed gas molecules on the chemically sensitive coating of QCM

Table 1  
Properties of AT cut Quartz crystal

Quartz Parameter	Value	Description
$\rho_q$	2651 Kg/m <sup>3</sup>	density of quartz crystal
$\eta_q$	9.27 * 10 <sup>-3</sup> Pa. s	viscosity of quartz crystal
$G_q$	2.93*10 <sup>9</sup> Pa	shear modulus of AT cut quartz crystal
$f_0$	10 MHz	resonant frequency of crystal
$\epsilon_{22}$	3.982*10 <sup>-11</sup> A <sup>2</sup> s <sup>4</sup> /kgm <sup>3</sup>	permittivity of quartz
$c_{66}$	9.2947 * 10 <sup>10</sup> N/m <sup>2</sup>	component of material property tensor for mechanical stiffness
$Z_{cq}$	8852147 $\Omega$	Characteristic impedance of quartz crystal

This sensor structure is similar to thin film sensors, with the QCR as the substrate. Thus, laws of diffusion as applied to thin film sensors are applied to the coated QCM along with kinetic analysis of the QCM. Coated QCM has been used in liquids as presented by Arnau et al. (2001), Rabe et al. (2003) and Lucklum et al. (1999). Its electrical equivalent circuit is represented by the Extended Butterworth Van Dyke model (EBVD) as proposed by Arnau et al. (2001) considering shear parameters as used by Johannsmann et al. (1992). The elements of the EBVD model are considered frequency independent as mentioned by Martin et al. (1991). Limited literature is published on use of QCM for nitroaromatic gas concentration estimation.

An AT cut quartz crystal in thickness shear mode was coated and placed in a test chamber of known volume. Adsorption of gas molecules occurs on the coated surface proportional to concentration, which increases the deposited mass. Kinetic analysis of QCM was combined with Diffusion Reaction Model (DRM) to develop the parametric model. Some values of the QCM considered for modeling are illustrated in Table 1 as presented by Arnau et al. (2001).

The equivalent circuit of the quartz crystal loaded with a finite viscoelastic layer contacting a semi-infinite viscoelastic medium is illustrated in Figure 2 and known as the

Extended Butterworth Van Dyke (EBVD) Model. Changes in the surface mass density of coating produce changes in the electrical impedance of the sensor.

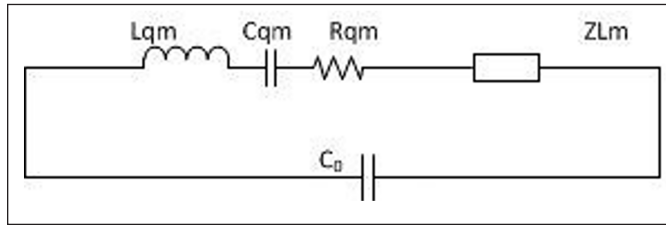


Figure 2. Circuit representation of the EBVD model

The complex electrical input impedance  $Z$  between terminals of loaded QCR can be expressed as:

$$Z = \frac{1}{j\omega C_0} \left( 1 - \frac{K_q^2}{\alpha_q} \cdot \frac{2 \tan \frac{\alpha_q}{2} - j \frac{Z_L}{Z_q}}{1 - j \frac{Z_L}{Z_q} \cot \alpha_q} \right) \quad [2]$$

Where  $\alpha_q$  = acoustic phase shift in quartz crystal,  $K_q^2$  = complex electromechanical coupling factor =  $K_q^2 = \frac{e_q}{\varepsilon_q c_q}$ . The characteristic quartz impedance  $Z_q = \sqrt{c_q \rho_q}$  where and  $c_q = \overline{c_{66}} = c_{66} + \frac{e_{26}^2}{\varepsilon_{22}}$  is the piezoelectric stress coefficient. The values of circuit elements of the EBVD model are given by  $R_m^q = \frac{(N\pi)^2 n_q}{8K_q^2 C_0 c_q}$ ,  $C_m^q = \frac{8K_q^2 C_0}{(N\pi)^2}$ ,  $L_m^q = \frac{1}{\omega_s^2 C_0}$  and  $C_0 = \frac{\varepsilon_{22} A}{d_q}$  where  $\omega_s$  is the series resonating frequency,  $d_q$  is the thickness of quartz disc and  $A$  is area of electrodes. The surface mechanical load impedance for a single coating which is equivalent to the motional load impedance  $Z_L$  exposed to a gas can be stated with equation [3] and proposed by Lucklum et al. (2006).

$$Z_L = j \sqrt{\rho_1 G_1 \tan \left( h_1 \omega \sqrt{\frac{\rho_1}{G_1}} \right)} \quad [3]$$

where  $h_1$  = thickness as shown in Figure 1 and  $\rho_1$  is density of deposited layer,  $G_1$  is complex elastic modulus of sensing layer and expressed as  $G_1 = G_1' + jG_1''$ ,  $G_1'$  where = Energy storage and  $G_1''$  = Energy dissipation in layer. Loss angle  $\delta_1$  is expressed as  $\tan \delta_1 = \frac{G_1''}{G_1'}$ . To analyze the response of QCM, the parameter change in resonant frequency needs to be measured and is expressed as equation [4].

$$\Delta f_s \approx \left( \frac{f_s}{N\pi} \sqrt{\frac{G_2'' \rho_2}{2\rho_q \bar{c}_{66}}} \left( \frac{\sqrt{1 + \tan^2 \delta_2} - 1}{\tan \delta_2} \right)^{\frac{1}{2}} + \frac{2f_s^2 \rho_s}{N\sqrt{\rho_q \bar{c}_{66}}} \right) \quad [4]$$

$G_2''$  is the shear contribution and  $\rho_2$  is the density of gas under test.  $\delta_2$  is the loss angle between sensing layer and medium under test. As the layer 2 is considered gas in the developed model, the EBVD model cannot be used for gas concentration estimation as the phenomenon of adsorption and desorption is not included. Also, as the EBVD model is a standard model, the performance of a newly developed model can be evaluated by comparing its results with the EBVD model. However, if the newly developed model is developed for a target gas, the EBVD model needs to be rearranged.

### Thin Film Sensors

Adsorption and desorption of gas molecules due to diffusion occurs on the chemically sensitive coating, resulting in change in electrical properties of the sensor. The sensor was modeled using DRM and configuration of the sensor is as shown in Figure 3, where 'x' is the thickness of the film. 'x'=L indicates that the thickness of the film is L.

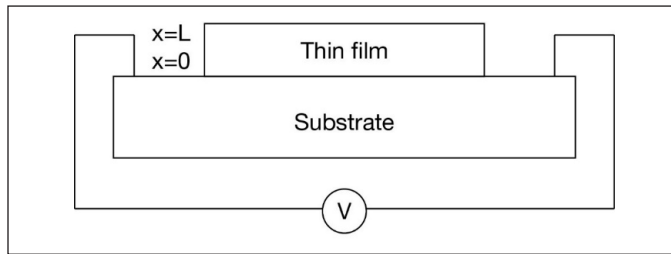


Figure 3. Thin film sensors

The gas adsorption to the surface of thin film sensors is based on Langmuir Isotherm and is expressed as  $A + S \xrightleftharpoons{k_f} AS$  where A, S and AS are the detected gas, the polymer film free surface area, and the occupied surfaces of the sensing film, respectively.  $k_f$  and  $k_b$  are the rate of forward and backward adsorption kinetics. Taking  $x$  as the depth of adsorption in the film,  $t$  as the time and  $\theta(x, \tau)$  as the fraction of occupied surfaces on sensing film, the diffusion reaction equation for species of gas 'a' was presented by Galic et al. (2006) and Gardner et al. (1995).

$$D \frac{\partial^2 a}{\partial x^2} - k_f a(1 - \theta)N + k_b \theta N = \frac{\partial a}{\partial t} \quad [5]$$

In equation [5], concentration of diffusing gas 'a' is a function of  $x$  and time.  $D$  is the diffusion rate and  $N$  is the density of film.  $L$  is the thickness of sensing film as shown in

Figure 3 and  $a_\infty$  is the maximum concentration of gas. Using the boundary conditions as  $t=0$ ;  $\theta = 0$  and  $0 \leq x \leq L$ , then at  $t > 0$ ;  $\frac{da}{dx} = 0$  at  $x = 0$  and  $a = a_\infty$  at  $x = L$ . Converting it to dimensionless form, an approximate analytical solution for linear diffusion in dimensionless form is expressed in equation [6].

$$\eta \frac{\partial \theta}{\partial \tau} = \kappa \lambda \gamma - \kappa \theta \quad [6]$$

Normalized gas concentration  $\gamma = \frac{a}{a_\infty}$ ;  $\tau$  is the dimensionless time parameter given by  $\tau = \frac{t}{t_{cycle}}$  where  $t$  is the time,  $t = t_{cycle}$  is the time for which sensor is exposed to gas.  $\eta = KN$  where  $K = \frac{k_f}{k_b}$ ,  $N$ = density of film and  $\lambda = Ka_\infty$ . The dimensionless depth of adsorption  $\chi = \frac{x}{L}$ ; and  $\kappa = \frac{k_f NL^2}{D}$ . The gas concentration profile  $\gamma(\chi, \tau)$  and occupied surfaces  $\theta(\chi, \tau)$  are expressed in equation [7] and [8] as proposed by Gardner et al. (1995) and Bartlett and Gardner (1996).

$$\gamma(\chi, \tau) = 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(\eta + 1/2)\pi\chi] \exp\left[-(\eta + \frac{1}{2})^2 \pi^2 \tau\right]}{(-1)^n (\eta + 1/2)} \quad [7]$$

$$\theta(\chi, \tau) \approx \lambda \gamma \quad [8]$$

This study summarizes that the surfaces occupied with gas molecules are dependent on the  $\gamma$ ,  $k_f$ ,  $k_b$ ,  $a_\infty$  and  $\rho_1$ .

### Model Development

The kinetic analysis is a study depending on the relative and absolute concentration of analyte with time. When the sensing layer is subjected to the gas under test, the adsorption progresses, resulting in increase of deposited mass and reduction in resonant frequency. The phenomenon is explained with the equation [9].

$$\theta(t) \propto \Delta m(t) \propto -\Delta f(t) \quad [9]$$

The occupied surface on the sensing film  $\theta(t)$  depends on the following parameters; viz. gas concentration, forward and backward reaction rate, maximum concentration of the gas under test in the test environment, density of sensing layer and the time for which

the sensor is subjected to gas. The  $\Delta m(t)$  is proportional to change in frequency, which in turn is expressed in equation [10].

$$\Delta m(t) \propto \frac{Im(Z_L)(t)}{\pi Z_{cq}} \quad [10]$$

Where  $Z_L$  is the acoustic load impedance given by equation [3] and  $Z_{cq}$  is the characteristic quartz impedance and calculated using the  $R_m^q, C_m^q, L_m^q$  and  $C_0$ . Applying the boundary conditions of depth of adsorption  $x$  as  $h_1$ , which is the thickness of sensing film and time for which the sensor is subjected  $t = t_{cycle}$ , the equation [9] is solved further. At  $t = 0$ ;  $\theta(t) = 0$ ; and  $0 \leq \text{depth of adsorption } x \leq h_1$ , then at  $t > 0$ ;

$$\frac{da}{dx} = 0; \text{ at } x = 0 \text{ and } t = 0; a = a_\infty \text{ at } x = h_1 \text{ and } t = t_{cycle} \quad [11]$$

$a$  is the concentration of the gas and  $a_\infty$  is the maximum gas concentration. From the equation of occupied surface used in the DRM and the kinetic analysis of the QCM, the equation [9] is solved with above stated boundaries and a parametric model of DRM and kinetic analysis of QCM is derived for estimating the gas concentration.

$$a(t) = \frac{C \cdot a_\infty f_0}{\lambda \pi Z_{cq}} \sum_{t=0}^{t=t_{cycle}} \frac{-Im(Z_L)(t)}{\Delta f(t)} \quad [12]$$

In the above model,  $\lambda = K a_\infty$ ,  $K = \frac{k_f}{k_b}$ ,  $Z_L$  is calculated as expressed in equation [7], where  $h_1$  is considered as  $16.61 \mu\text{m}$ .  $G_l$  is complex elastic modulus of sensing layer and  $C$  is a fitting constant.  $\Delta f(t) = f_L(t) - f_0$ , where  $f_L$  is the resonant frequency of the crystal when subjected to gas at  $t=0$  to  $t = t_{cycle}$  and  $f_0$  is the resonant frequency of unperturbed quartz crystal.  $G_l' = 10^9 \text{ Pa}$  and  $G_l'' = 10^2 \text{ Pa}$  and considered same for the above model.

The following assumptions are done while developing the parametric model

- Surface load mechanical impedance can be represented with the density and thickness of the sensing layer along with shear parameters
- The layer deposited is very thin and is free of any prior adsorption
- Homogenous adsorption of gas molecules throughout the surface
- Adsorption and desorption cycle time are approximately same with desorption starting by step change in gas concentration to zero

## Experimentation

A comprehensive study was done from the work of Cui et al. (2016), Palaniappan et al. (2008), Özmen et al. (2006), Yang and He (2016), Erbahar et al. (2011), Li et al. (2007) and Ramdasi and Mudhalwadkar (2018) for identifying the materials of sensing layer. As

the performance of polymers with metal oxides for explosive detection was prominent, polyaniline (Sigma-Aldrich, India) based sensing layer with palladium metal powder (Ottokemi, India) for selectivity enhancement was used. The following procedure was adopted to develop the chemically sensitive layer. A micro balance was used to weigh the powders accurately. The weight of the powders depends on the pre-decided ratio of the mixture of powders to achieve a higher selectivity and sensitivity. The weight ratios decided for the sensor was a mixture of selective material powder (6%) and sensitive material powder (94%). The sensitive powder was a mixture of Polyaniline (65%) Tungsten Oxide (Research-Lab Fine Chem Industries, India) (35%). As the powders needed to mix properly and micro or nano granules to form, severe pulverization of the mixture was done. The pulverized powder was mixed with 2-3 drops of glycerin (Sigma-Aldrich, India) which acted as a binding agent. 1-2 drops of Dimethyl Sulfoxide (Sigma-Aldrich, India) were also added, which acted as a chemical agent. Small part of the mixture was carefully placed on the crystal with a micropipette and the crystal was then sintered at 80°C in an oven for 40 minutes. It was observed that if the mixture deposited on the crystal becomes excess, the crystal ceased to resonate. The density of the layer was calculated using formula for density of mixture and accounts to 0.804 g/cm<sup>3</sup>.

Figure 4 shows the uncoated 10 MHz Au coated quartz crystal (971-00006, GAMRY Instruments, USA) used for experimentation while Figure 5 shows the crystal after drop coating. Figure 6 shows the coated crystal after sintering. The distance between the two terminals is 9 mm, which is approximately equal to the quartz crystal resonators.

The  $\alpha_\infty$  was calculated using the upper explosive limit of NB and density of NB was 1.2 g/cm<sup>3</sup>. The volume of test chamber was 560 ml. The forward and backward reaction rate was 0.65034/s and 0.45563/s respectively as suggested in the literature. The thickness of the crystal was 0.00016 m and electrode area was 0.293 cm<sup>2</sup>. The standard crystal parameters proposed by Arnau et al. (2001) were considered and are detailed in Table 1. The experimental setup included an air tight chamber with inlet and outlet connections

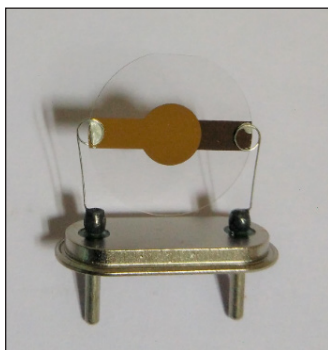


Figure 4. Uncoated AT cut 10 MHz quartz crystal



Figure 5. Crystal after drop coating



Figure 6. Coated crystal used for experimentation after sintering



for gas under test. The chamber was fitted with a cuvette which held the coated QCR connected to a computer via the Electrochemical Quartz Crystal Microbalance (EQCM) (eQCM10M, GAMRY Instruments, USA). The resonant frequency of 10 MHz changes to 9.995 MHz after deposition of the chemically sensitive layer. The concentration of gas was calculated for a variation in resonant frequency from 9.995 MHz to 9.992 MHz for a cycle time of 600 seconds.

### Model Validation by Experimental Method

The developed model was validated experimentally by subjecting the coated QCM to a varying concentration of NB from 30 ppb to 1000 ppb. The response of the coated QCM was acquired and analyzed using the GAMRY EQCM resonator software in the Echem analyst environment. For this, the coated QCM was placed in an air-tight chamber of 560 mL volume, in a cuvette as illustrated in Figure 7 and was exposed to known concentration of NB via a pump (20K series, Boxer Pump, UK) with speed set to 400 mL/ min. If the speed of the pump was lower, the sensing layer required a higher time to saturate, thus increasing the response time of the sensor. As the sample gas came in and left the gas chamber, the pressure in the gas chamber was assumed to be at atmospheric value. The complete setup of experimentation is presented in Figure 8.

To generate the desired concentration, the calculated amount of volatile compound was introduced in liquid phase in an air tight container. The compound was allowed to mix with the air in the container. The following procedure was adopted to calculate the volume to be injected in liquid phase.

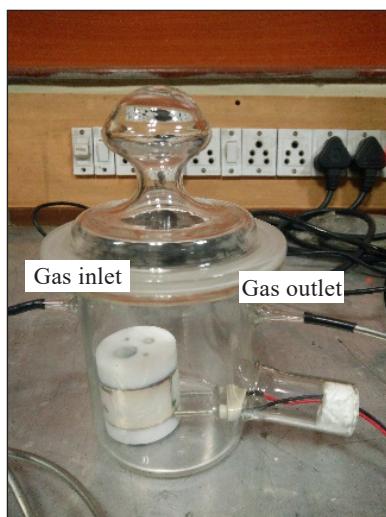


Figure 7. Quartz Crystal placed in cuvette and exposed to NB



Figure 8. Experimental setup for coated Quartz Crystal Microbalance

- a. Calculate the density  $\partial$  in g/litre using the following formula and values

$$\partial = \frac{P.MW}{R.T} \quad [13]$$

where P is the standard atmospheric pressure, 1 atm;

MW is the molecular weight of compound (NB=123.06 g/mol);

R is the Universal gas constant in L.atm/mol.K = 0.0821

T is the temperature in degree Kelvin

- b. Using the formula, calculate the volume to be injected in liquid phase

$$V_{liq} = \frac{V_{gas} \cdot \partial}{\rho} \quad [14]$$

where  $V_{gas}$  is the required volume of compound in gaseous state;

$\rho$  is the density in g/cm<sup>3</sup> (NB= 1.2)

The change in resonant frequency and the corresponding addition in mass was noted using the e-QCM software and its corresponding concentration in Parts Per Billion (ppb) was calculated using standard formula.

### Model Validation by Analytical Method

The results of the derived model were compared with the EBVD model. The equation for change in resonant frequency was modified for measuring gas concentration considering volume of test chamber and density of NB and stated in equation [15].

$$m(t) = \frac{2\rho_q \bar{c}_{66}}{G_2''} \left( \frac{N\pi V^2}{f_0} \right)^2 \left( \frac{\tan \delta_2}{\sqrt{1 + \tan^2 \delta_2} - 1} \right) \left( \Delta f(t) + \frac{2f_0^2 \rho_1 h_1}{N\rho_q \bar{c}_{66}} \right)^2 \quad [15]$$

In the equation,  $\delta_2$  is the loss angle between the sensing layer and gas layer, considered as 1.57 and  $G_2'' = 1.3 \times 10^3$  Pa. The deviation in resonant frequency due to adsorption of gas molecules on the chemically sensitive coating is considered as 0 to 3000 Hz.

### RESULTS AND DISCUSSION

A parametric model for a coated QCM is derived using DRM and kinetic analysis of QCM. The results are compared with the rearranged equation of EBVD model.

As the DRM is governed by adsorption, a study of the diffusion of gas molecules due to adsorption was done. Figure 9 shows the normalized concentration during adsorption for chemically sensitive coated sensor. Increase in normalized concentration was observed when the depth of adsorption in the coating increased for varying time cycles.

Figure 10 shows that as the time for which the sensor was exposed to the gas under test progresses, more surface of the sensing layer was occupied due to adsorption of gas, till the surface neared saturation. Equation [8] explains this phenomenon, which is further used for kinetic analysis of the coated QCM. This phenomenon was also observed during the experimental validation. When the coated QCM was exposed to gas, the sensing layer surface experiencing adsorption increased, which in turn increased the mass deposited on the layer. This ultimately resulted into a reduced resonant frequency of the coated quartz crystal. The developed parametric model was validated experimentally as well as with the rearranged EBVD model. Figure 11 illustrates the response of the developed parametric model for detection of NB along with experimental and analytical validation. The developed model and the experimentation indicate that, for a 10 MHz crystal coated with a sensing layer for NB, the deviation in the resonant frequency is a measure of concentration of the gas. Thus, the X axis of Figure 11 represents the deviation in the frequency for 10 MHz crystal and the Y axis indicates the corresponding gas concentration in ppb. The graph is a representation of the measurement system results for lower concentration range of NB, from 30 ppb to 1000 ppb. The figure shows the actual concentration of NB in parts per billion for the respective change in resonant frequency for the developed model, the modified EBVD model and experimentation. The graph exhibits a nonlinear relation with the deviation in resonant frequency due to nonlinear nature of the phenomenon of adsorption. For a maximum deviation in frequency of 3000 Hz, the concentration of NB at  $t = t_{cycle}$  is 978 ppb for EBVD model while it is 976 ppb for the derived parametric model for an actual concentration of 1000 ppb. The developed model thus performs with an accuracy of 74% for NB concentrations above 300 ppb. As the EBVD is an electronic model, it lacks the effect of adsorption, due to which the nature of the graphs of both models is different.

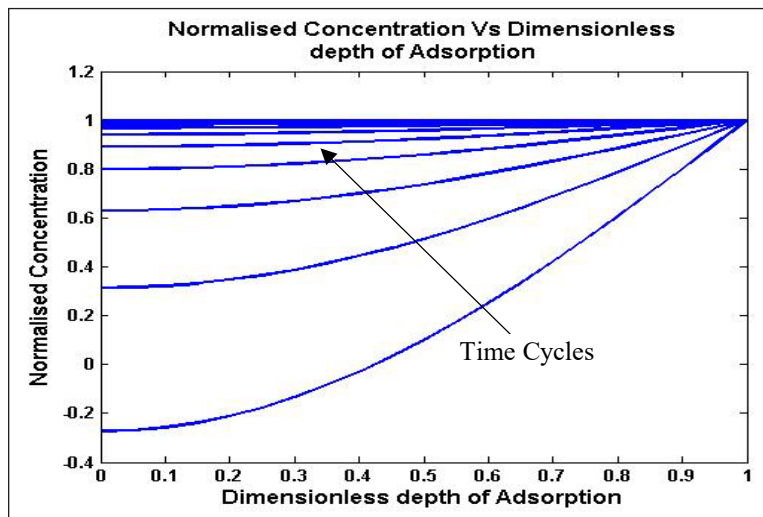


Figure 9. Normalised concentration vs Depth of adsorption

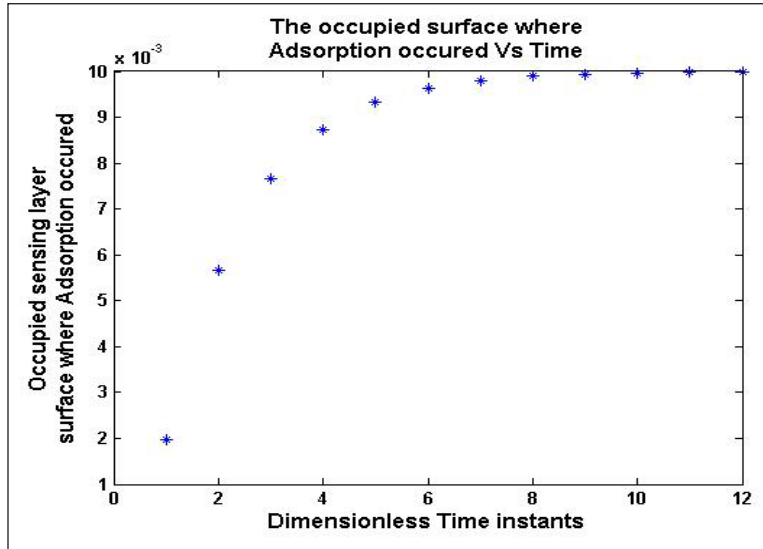


Figure 10. Occupied Surface vs Time for which sensor was exposed to gas

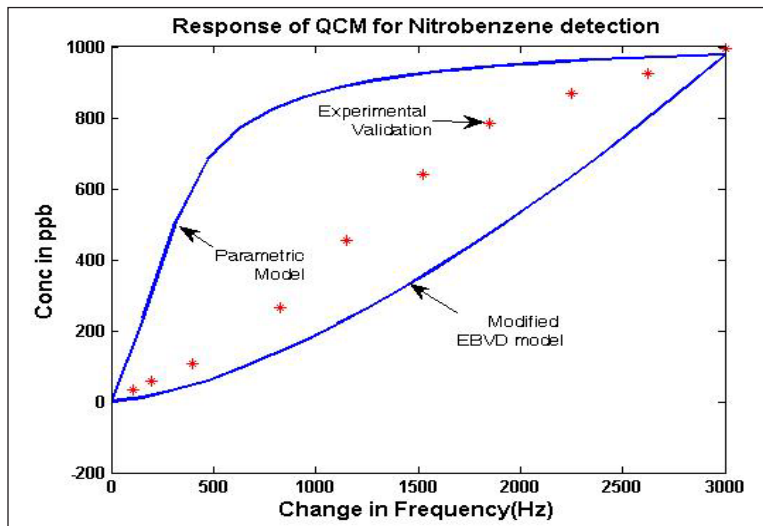


Figure 11. Concentration estimation of nitrobenzene using parametric model and validation results with experimental and analytical method

Figure 12 shows response of the coated QCM when subjected to a concentration of 800 ppb nitrobenzene, as observed on the EQCM software. The EQCM software is a powerful tool to analyze the behavior of the quartz crystal, when subjected to deposition of mass on the electrode surface. The X axis represents the time instants, when the coated QCM is subjected to gas. The graph has two Y axis, one axis represents the deviation in the resonant frequency of 10 MHz crystal, indicated by the 'dF series'. The second Y axis indicates the mass deposited on the quartz crystal in  $\mu\text{g}$ , indicated by  $\Delta M$ . The observed mass is 2.75

$\mu\text{g}$  in the volume of 560 ml. The concentration in ppm is calculated by first calculating the mass in one-liter volume and then using equation [16]. Standard atmospheric temperature and pressure are used for calculations.

$$\text{Conc}_{\text{ppm}} = \frac{\text{mass per liter} * \text{Atmospheric Pressure}}{\text{Molecular wt of NB in g/mol}} \quad [16]$$

As the process of adsorption and desorption are nonlinear, a fitting constant is incorporated in the model. The sensing layer is chemically sensitive to NB and developed from Polyaniline, Tungsten Oxide, Palladium and Dimethyl Sulfoxide.

The explosives exhibit nitroaroma, however reliable sensors are not available to detect nitroaroma in low level of detection, typically ppb. This model uses the advantage of mass sensitivity of the quartz crystals to detect small changes in the mass deposited on the quartz surface. The response time of the sensor is observed as 6.5 seconds while the recovery time is 180 seconds. Higher response and recovery time is a characteristic of thin film sensors, which is observed in the developed sensor also, due to its functional relevance with thin film sensors. The change in deposited mass is an effect of adsorption of gas molecules on the sensitive layer surface. With detailed study and knowledge of sensitive coating materials for gas detection, exact coatings of chemically sensitive layers can be developed by different techniques. This model than can assist in estimation of gas concentration and can be further extended to decide the presence of explosives. The timely detection of explosives can prevent heavy losses to mankind and nature.

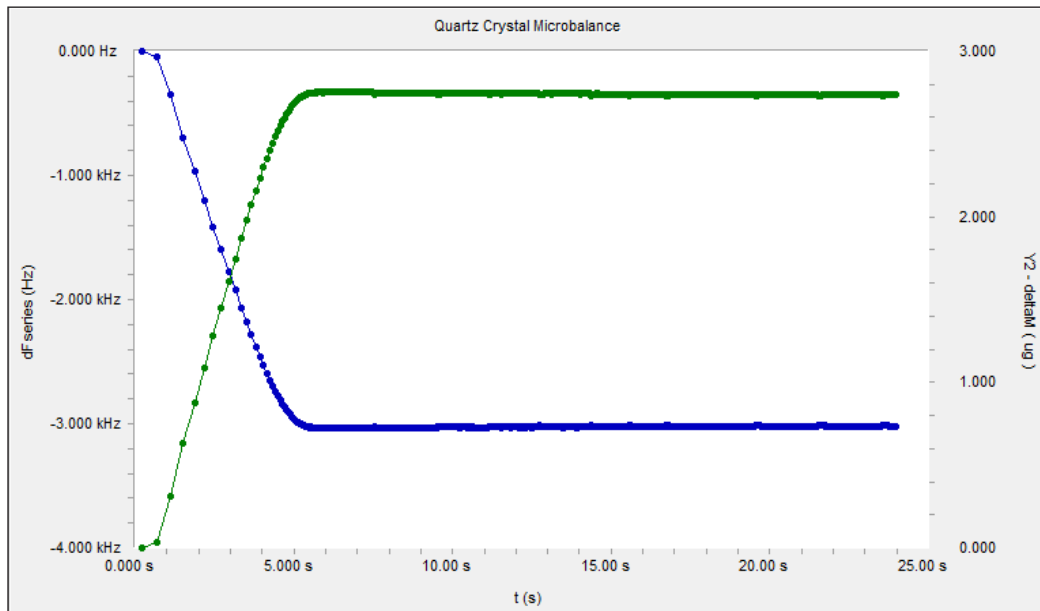


Figure 12. Response of coated QCM for 800 ppb nitrobenzene

## CONCLUSION

A parametric model for detecting NB was developed for a 10 MHz AT cut quartz crystal deposited with a chemically sensitive coating. The parameters of cycle time, density and thickness of sensing layer were considered for modeling along with standard crystal parameters. The results of the developed model were compared with the rearranged equation of Extended Butterworth Van Dyke Model. The model was validated experimentally for concentration of NB ranging from 30 ppb to 1000 ppb. For concentrations lower than 300 ppb, the derived model exhibits maximum deviation, however, for concentrations above 300 ppb, the derived model estimated the concentration of NB with an accuracy of 74%. The mass sensitivity and advantage of chemical selectivity using chemically sensitive layer was combined in the derived model. This model can assist researchers in the selection of elements of the chemically sensitive coating for a target gas and leads one step closer to timely detection of explosives.

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