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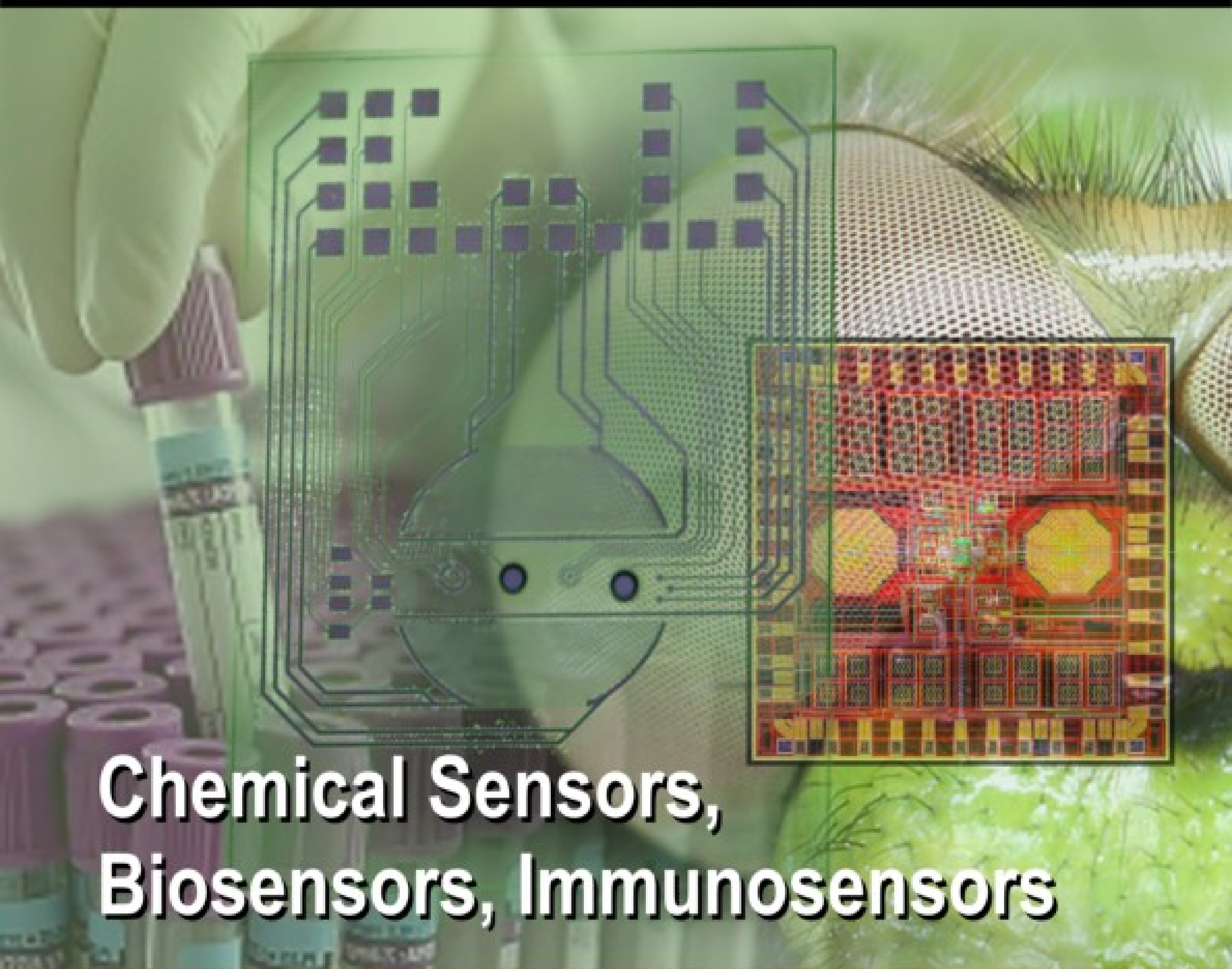

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Epoxy Resin Modified Quartz Crystal Microbalance Sensor for Chemical Warfare Agent Sulfur Mustard Vapor Detection

***Rajendra BUNKAR, K. D. VYAS, V. K. RAO, Sunil KUMAR, Beer SINGH, M. P. KAUSHIK**
Defence Research and Development Establishment, Jhansi Road, Gwalior, M.P., 474002, India
Tel.: +91-07512341960, fax: 0751-2341148
E-mail: rajbunkar.drdo@gmail.com

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Abstract: An epoxy resin polymer coated quartz crystal microbalance (PC-QCM) is used for detection of sulfur mustard vapor (SM). When SM vapor is exposed to PC-QCM sensor frequency shift is observed. The response of the sensor in ambient condition is 554 Hz with ±10 % variation upon exposure of 155 ppm of the SM concentration. The observed response loss is nearly 40 % over the period of 15 months. The response of the sensor is higher for SM than compare to structurally similar chloroethyl ether (CEE) and other interferences. *Copyright © 2010 IFSA.*

Keywords: Epoxy resin, QCM sensor, Sulfur mustard, Response

1. Introduction

The chemical warfare agents (CWA) are defined as chemical substances that have the potential to cause physiological changes in living organisms. The CWA comes under lethal class of compounds that threat to military personnel in the battlefields and civilians in public places [1]. In order to identify such threats and counter the tactical operations an effective detection system is necessary in contemporary scenario. There are several approaches for detection of CWA specially nerve agents and their simulants like dye solubility, flame photometry detector (FPD), ion mobility spectrometry and QCM based detection etc [2 – 4]. On the other hand the detection of SM and organosulfur compounds is less explored in the literature. The SM is known as king of chemical warfare agents and it causes metabolic and genotoxic effects in living organisms hence its detection is essential [5].

The QCM sensors used as chemical and biological sensors under ambient conditions on application of chemoselective coating on quartz crystal (QC) surface [6-7]. The polymer coating is preferred choice for sensors because their physicochemical properties can be tailored according to the applications [8]. In this present study we report on the use of commercially available epoxy resin as sensitive coating material for SM detection by QCM sensor.

2. Experimental

2.1. Reagents and Apparatus

Bis(2-chloroethyl)sulphide (Sulfur mustard) was synthesized in the laboratory and found more than 99 % pure by GC/GC-MS analysis. The epoxy resin of Araldite make was purchased from Huntsman advanced materials, Mumbai, India. The solvents used in this study were AR grade (99.99 % purity, Sigma Aldrich). **Caution:** Sulfur mustard is a blistering agent and potential vesicant so it should be handled inside the fuming hood by wearing hand gloves.

The PC-QCM sensor has been evaluated for its sensitivity for SM by using experimental setup shown in Fig 1. A piezoelectric crystal interfaced with oscillator circuit, frequency counter and computer was housed in a glass assembly. Nitrogen gas flow was maintained by using mass flow controller (Sierra instruments, USA). The frequency drift (ΔF) was monitored with a frequency counter (Aplab 1.3 GHz frequency counter 1122). The saturated diffusion concentration of exposed vapors of sulfur mustard and other molecules used in this study were calculated by using reported methods [9-10].

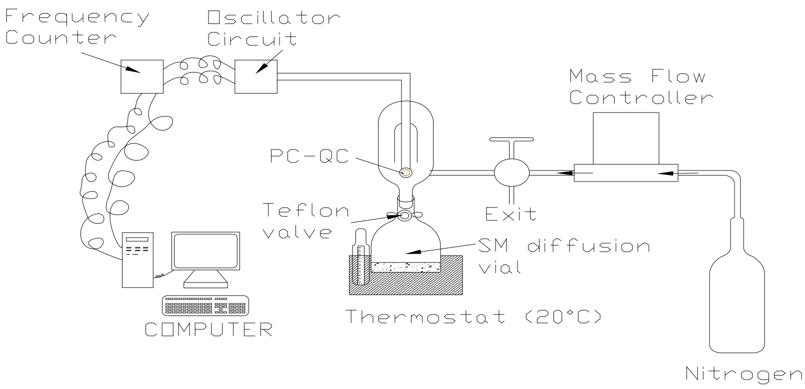


Fig. 1. Schematic diagram of the sulfur mustard detection system.

The formulas used for these calculations were as

$$P_{20} = (1013/760) \times 10^{c} , \quad (1)$$

where P_{20} is the saturated vapor pressure and the term C was calculated by

$$C = (2.8808) - [\{(a_n \times t_b + b_n) (t_b-20)\} / (296.1 - 0.15\, t_b)]$$

The vapor density (d_m) and concentration in ppm were calculated by following formulas

$$d_m = 1 + 34 \text{ X } P_{20} X\, 10^{-6} (M-29) \quad (2)$$

$$C_{ppm} = (C_{mg/m3} \text{ X } 24.4) / M \quad (3)$$

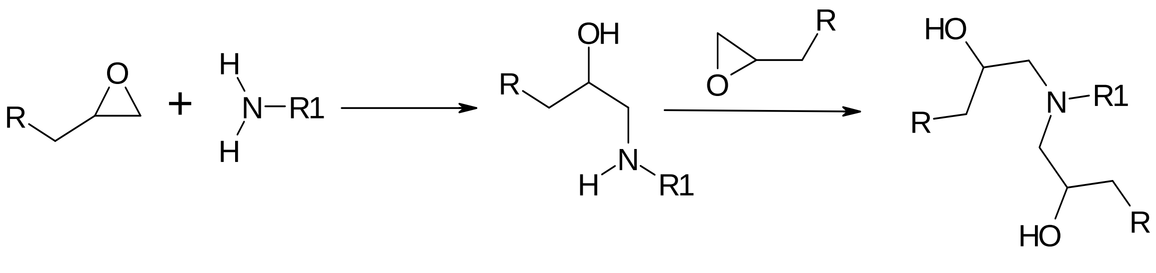
Here a_n and b_n are Van der Waals constants, t_b is the boiling point and M is the molecular weight of the molecule. The PC-QCM sensor was initially purged by N_2 for 10 minutes to get stable base line. The time dependent frequency shifts of sensor were recorded by exposing of SM vapor in response cycle and alternatively purging of N_2 (300 cc/min) in recovery cycle. These alternate cycles were repeated eight times to get the overall response pattern and to investigate the reversibility of sensor.

2.2 Deposition of Sensitive Layer

A spherical quartz piezoelectric crystal (AT–cut, basic resonant frequency 10 MHz, 7 mm diameter, 0.2 mm thickness possessing circular gold electrodes) was coated with epoxy resin. The drop coating method was employed to deposit the sensing film on QC [11]. A DMF solution containing 2:1 stoichiometric ratio of epoxy resin to curing agent was used to deposit it on to the QC surface. The coated crystal was oven dried at 100°C for one hour and it was termed as polymer coated quartz crystal (PC-QC). The 4 kHz coating thickness of PC-QC was maintained by washing it by DMF followed by drying.

2.3. The Epoxy Resin Material

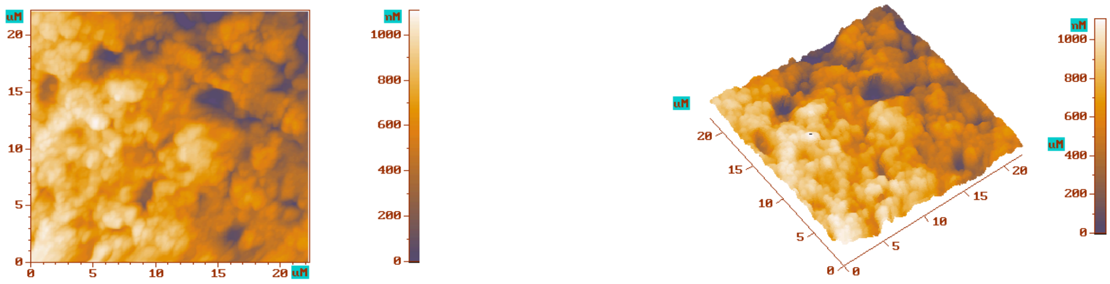
The epoxy resin is diglycidyl ether of bisphenol A and epichlorohydrin monomers. It was selected for present study because of structural compatibility for SM sensing, tendency to form stable film, relatively higher glass transition temperature (T_g) and commercial availability. The T_g of epoxy resin polymer employed for sensor applications determines the extent of sorption favorable glassy state (locked chain conformation) than compare to elastomeric state at particular temperature. The reaction between curative agent and epoxy resin yields extensive hydroxy groups into the framework (Scheme 1). The chemical activity of the polymer is least affected by temperature because of its high T_g [12]. The higher Tg of polymer is preferred because the sorption active glassy state also remains available in more extent at higher operating temperatures.



Scheme 1. The reaction of epoxy resin and curing agent which yields surface hydroxy groups in resin framework.

3. Results and Discussion

The three dimensional Atomic force microscopic image of the epoxy resin film is shown in Fig. 2 (5600LS AFM, Agilent Technologies). The color intensity shows the vertical profile of the membrane surface, with light regions being highest points and dark regions being the depression and pores. The micrograph shows homogeneous surface morphology with depressions, which means the porous and irregular surface topology. It might favor the interaction with SM vapors and further responsible for sensitivity.



(a) (b)

Fig. 2. AFM image of epoxy resin film (a) 2D image; and (b) 3D image.

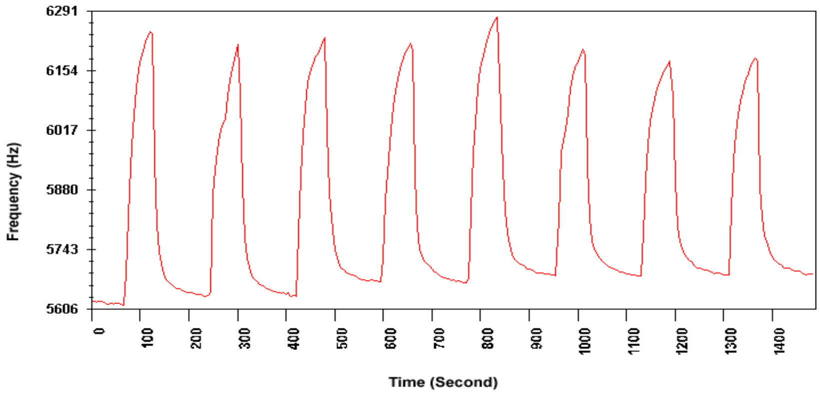
The response of a PC-QC device for sulfur mustard vapors is shown in Fig. 3a. The response pattern is obtained against time (seconds) and frequency (Hz) at X axis and Y axis respectively. The response of the sensor is calculated in terms of hertz by averaging height of the maximum and minimum signal. It is interesting to note that the rapid, consistent ~ 554 Hz (±10 % variation) response is observed upon exposure of SM vapor for 60 seconds on PC-QCM sensor. The observed small base line variation might be attributed to the presence of trace amount of SM on PC-QC surface after recovery cycle. However the sharp change in frequency and attainment of the initial frequency value clearly demonstrates that the PC-QCM sensor shows rapid, reversible and high response. The sensor is tested at different exposure times and same concentration as the desired SM vapor concentration is not attained because of low vapor pressure and higher toxicity. The better reversibility is observed at 60 seconds of exposure time.

The detection of HD was also reported by using four 158 MHz SAW single delay line sensors [13]. The sorbent interface polymer used for this detection were poly (epichlorohydrin) and ethyl cellulose (abbreviated as PECH and ECEL respectively) each on a separate sensor array. This work reports that the PECH material is more sensitive than compare to ECEL and has shown steady state response of 200-300 Hz at 2 mg/m^3 concentration. In present work we report the single epoxy coated QCM based detection of the SM in ambient condition. The sensor shows good sensitivity and reproducibility in experimental condition.

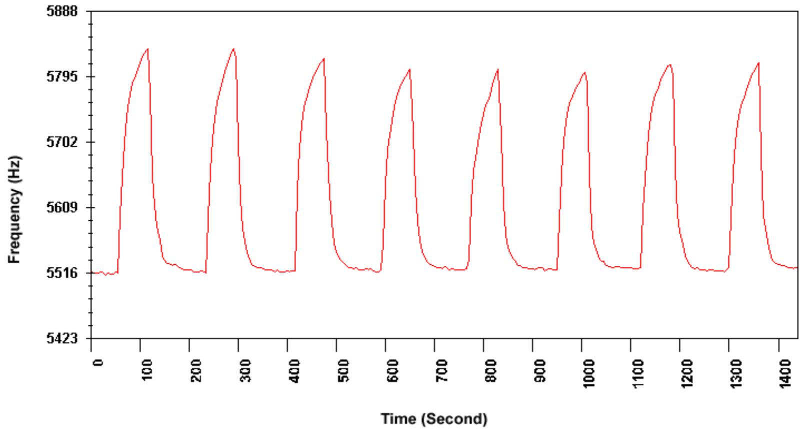
The reason of sensing might be attributed with the mass change and subsequently the frequency change of QC because of cumulative effect of various interactions between SM and epoxy film. The possible dipolar-dipolar, coordinate and Van der Waals interactions between SM and film are depicted in Scheme 2. The coordinate interaction is expected between lone pair containing nitrogen atom of the resin and vacant d orbital possessed by sulfur of the SM. The coordinate interaction is considered as weak interaction because of steric factors. Further the absorption of the SM into the epoxy resin polymer framework provides the basis of the higher detection efficiency of the PC-QCM sensor.

3.1. Sensitivity to Interference

The selectivity of the sensor was tested in presence of various interferences like chloroethyl ether (CEE), carbon tetrachloride (CTC), acetone, ethanol and toluene at saturation concentration. The vapor concentrations of each molecule (in ppm) are mentioned in Table 1. The Fig. 4 shows the response of sensor at saturation vapor concentration of SM, CEE, CTC and ethanol etc. The sensor shows higher response for SM than compare to CEE. It might be because of additional coordinate interaction between epoxy and SM (Scheme 2b). Further this type of interaction is not possible between CEE and epoxy. It clearly reveals that coordinate interaction plays a prominent role for higher sensitivity of the sensor.

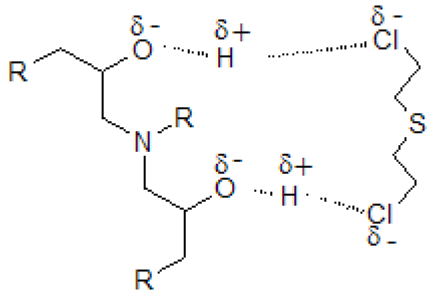


(a)

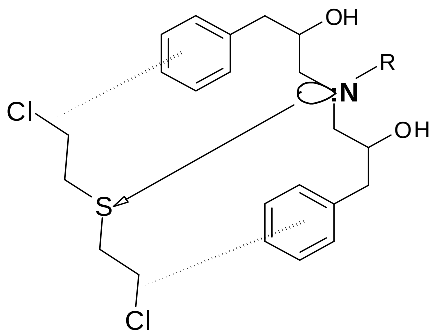


(b)

Fig. 3. Real-time frequency shift (Response) measurement of PC-QCM sensor for SM detection (a) Initial; and (b) After fifteen months.



(a)



(b)

Scheme 2. The probable interaction of SM and resin film through (a) hydrogen bond; and (b) the Van der Waals and weak coordinate bond interaction.

Table 1: Determination of Saturated vapor concentrations of various molecules.

No.	Molecule [a]	M.W.	Group No. (n)	a_n	b_n	t_b (°C)	Saturated Vapor Pressure[p_{20}] (in mbar)	Vapor density (d_m)	Concent-ration (ppm)
1	**SM**	159	20	0.0021	4.54	217	000.19	1.01	**155**
2	**CEE**	143	2	0.0021	4.54	178	001.36	1.01	**172**
3	**Toluene**	92	2	0.0021	4.54	111	028.27	1.11	294
4	**Acetone**	58	3	0.0021	4.77	56	243.16	1.24	521
5	**CTC**	154	4	0.0022	5.0	76	094.19	1.40	222
6	**Ethanol**	46	7	0.0023	5.67	78	063.68	1.04	552

Footnotes: [a] [*SM = Sulfur mustard, CEE = Chloroethyl Ether, CTC = Carbon Tetrachloride*], a_n, b_n *and* t_b *are Van der Waals's constants and boiling point of* n^{th} *group substance respectively.*

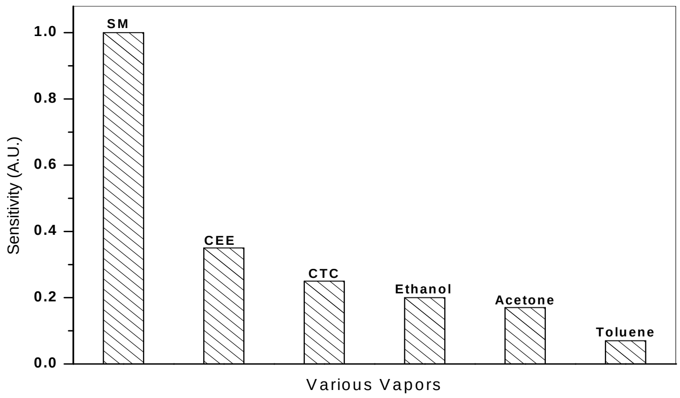


Fig. 4. Response of sensor for sulfur mustard and other interference vapors.

3.2. Stability of the Sensor

The reproducibility studies of the PC-QCM sensor is performed at different time interval. After ageing for fifteen months the sensor shows 310 Hz response with nearly 40% response loss and negligible base line drift (Fig. 3b). The observed loss may be attributed to the deterioration of the polymer coating after certain period of time [8].

4. Conclusion

The commercially available epoxy resin coating for QCM sensor was used to investigate vapors sensitive properties to SM and other interferences. The sensor shows 554 Hz response to the 155 ppm concentration of the SM vapor. The loss of stability was observed about 40% after fifteen months of coating. The sensor shows more sensitive to SM vapor than compare to other saturated interfering vapors. Thus epoxy resin is a very promising material which has great potential to work as a sensor material for detection of SM vapors.

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