Application of Polymer-Coated Quartz Crystal Microbalance (QCM) as a Sensor for BTEX Compounds Vapors

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ABSTRACT: A sensor based on the technique of a quartz crystal microbalance (QCM) was developed for the detection of organic vapors such as benzene, toluene, ethylbenzene, and xylenes (BTEX compounds). Detection was based on the adsorption of organic vapors on a thin layer of polydimethylsiloxane (PDMS) coated at the surface of AT-cut gold-coated quartz crystal electrodes. The frequency shifts due to the sorption of BTEX compounds were measured. Calibration graphs were constructed by plotting the frequency changes (ΔF/Hz) against the concentration of organic compounds. Using this method, the detection of these organic vapors was carried out at the ppm level. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1062–1066, 2001

Key words: polydimethylsiloxane; quartz crystal microbalance (QCM); sensor; BTEX compounds

INTRODUCTION

For many years, vapor sensors based on piezoelectric devices, such as thickness shear mode (TSM), surface acoustic wave (SAW), and quartz crystal microbalance (QCM) coated with nonconducting, nonvolatile liquids or polymers, have been described as gravimetric sensors.[1–5] In the piezoelectric devices, the frequency is known to decrease in response to an increase in mass on the sensor surface due to the adsorption of different chemicals. When small amounts of mass are adsorbed at the quartz electrode surface, the frequency of the quartz is changed according to the well-known Sauerbrey equation[6]:

$$\Delta F = -2f_0^2 \Delta m / A (\mu_g d_g)^{1/2}$$

where f_0 is the original oscillation frequency of quartz crystal; μ_g, the shear modules of the quartz; d_g, the density of the quartz; A, the surface area of the quartz plate undergoing oscillation; and Δm, the mass changes corresponding with the frequency change (ΔF).

The liquid or polymer usually concentrates vapor molecules from the gas phase by adsorption mechanism. This has been the basis for a series of novel studies[7–13] for the detection and determination of organic chemicals in recent years.

The early work of Edmonds and West[4] in the development of the piezoelectric monitor for the detection of organic gaseous pollutants included the measuring of chloroform and hexane using coated piezoelectric crystals. Dithizone and tri-*n*-octylphosphine oxide (TOPO) were tested[5] as coating materials to detect toluene diisocyanate (TDI) at the 2-ppm level. Using pattern-recognition techniques, the method provided a sensor system that could be either selective or sensitive for toxic organophosphorous compounds. More re-
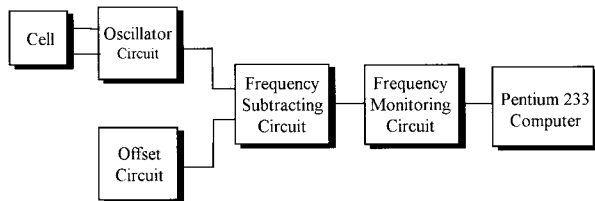
Figure 1 Schematic diagram of QCM instrument.

cently,[14] an AT-cut quartz crystal resonator coated with polyethylene (PE) film satisfactorily detected hydrocarbons at the ppm level. Small aromatics (benzene, toluene) and chlorinated (trichloroethylene, perchloroethylene) vapors were also detected by the QCM method.[15] In the current investigation, we considered the determination of some organic vapors such as benzene, toluene, ethylbenzene, and xylene isomers using QCM.

These chemicals that are generally referred to as the BTEX compounds are common contaminants in ground and surface water[16] and some are even suspected carcinogens. The chemicals were previously determined using different methods such as solid-phase microextraction (SPME) and Raman spectroscopy.[16] It was shown[17,18] that polydimethylsiloxane (PDMS) has a high affinity for aromatic organic compounds such as benzene and toluene and has been used in solid-phase microextraction as the stationary phase for extraction of aromatic organic compounds.[18,19] Therefore, this article is a report on the feasibility of using quartz crystals coated by PDMS to detect BTEX compounds.

EXPERIMENTAL

Materials

Benzene, toluene, ethylbenzene, and xylenes (BTEX), PDMS OV1, chloroform, and other chemicals were purchased from Merck (Germany) and used without further purification.

Instrumentation

Figure 1 shows a block diagram of the QCM setup used in this work. The cell comprised a 10-MHz AT-cut quartz crystal sandwiched between two vacuum-deposited gold electrodes (International Crystal Manufacturer, ICM, Oklahoma City, OK). The oscillator circuit used was based on that designed by Bruckenstein and Shay.[20] However,

some modification of the original design was also carried out to improve mass sensitivity and stability.[21]

In this design, the oscillation frequency of the QCM crystal was measured with respect to a reference crystal. The output was sent directly to a frequency countercircuit that allows the frequency change to be recorded *in situ* in a Pentium 233 IBM compatible computer. The circuit could also monitor the oscillation frequency of working and reference crystals. A subtracting circuit was also used in conjunction with the circuit to measure the frequency shift of the working electrode (due to any mass change) with respect to the reference electrode.

Film Preparation

A solution-casting method was used to cast polymer film on the top of the quartz crystal electrodes. The gold-coated quartz electrode was coated using a 5-μl solution of PDMS in chloroform (0.5% w/v). The film thickness varied corresponding to the polymer solution volume. In using a 5-μL solution (0.5% w/v), a typical thickness of 500 nm was obtained.

Adsorption/Desorption Setup

All sensing studies were carried out in a home-made cell (Fig. 2). A Hamilton syringe was used for the injection of organic compounds (Fig. 2). To desorb the organic compounds out of the electrode (regeneration of the sensor), a flow of air was purged through the cell. The backshift of the frequency to its initial position was taken as an indication of full desorption. The air stream was
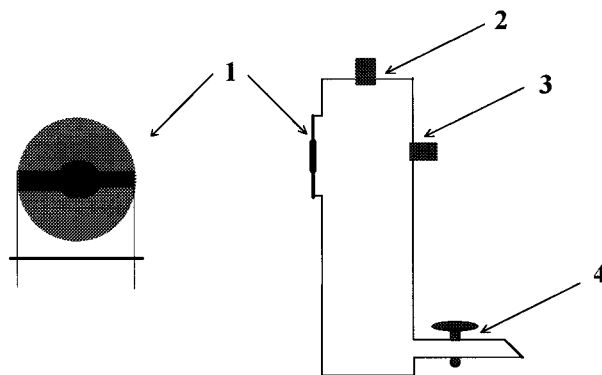
Figure 2 Measuring cell: (1) quartz crystal; (2) sample injector; (3) injector for polymer coating and air output; (4) air input.
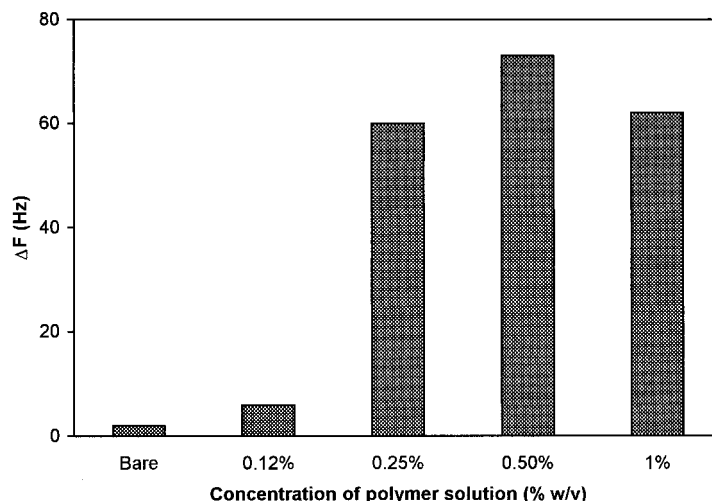
Figure 3 Frequency shifts of a quartz crystal electrode coated by PDMS films obtained from 0% (bare), 0.12%, 0.25%, 0.5%, and 1% (w/v) solutions of PDMS in chloroform: Note that all responses were obtained upon exposure to 15 ppm benzene.

passed through a gas drier container containing calcium sulfate prior to the desorption experiments.

RESULTS AND DISCUSSION

A crystal was coated using a 5-μL solution of various concentrations of PDMS/chloroform to obtain the optimum thickness. The polymer-coated crystal was exposed to a constant concentration of BTEX compounds, and the frequency shift due to the adsorption of the compound was measured as a function of time. Figure 3 is a frequency-shift response of a crystal with a different amount of PDMS obtained upon exposure to the constant concentration of benzene. The maximum frequency shift was recorded for the crystals coated using a 0.5% polymer solution (Fig. 3). It was also found that the film produced by a higher concentration of PDMS was less uniform in thickness. This effect can be experimentally verified since the response obtained for thicker films was not reproducible. Although the thinner films (e.g., coated by 0.12 and 0.2% solutions of PDMS) were uniform in thickness, the frequency shift (and
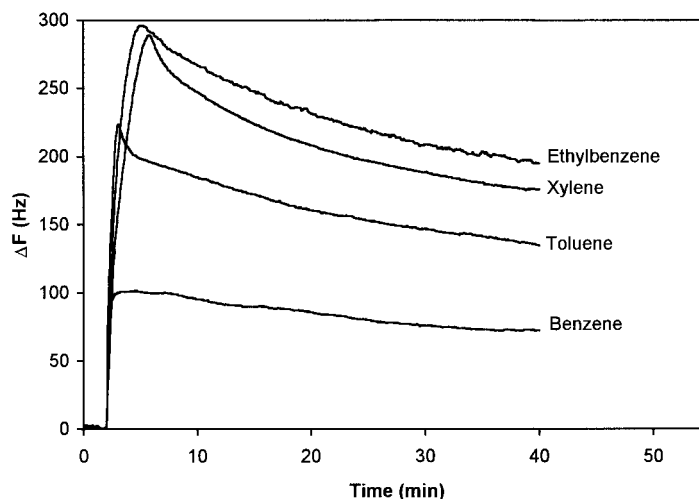
Figure 4 Time-dependent frequency changes of the quartz crystal-coated (by PDMS) electrode during exposure to the 15 ppm BTEX compounds.
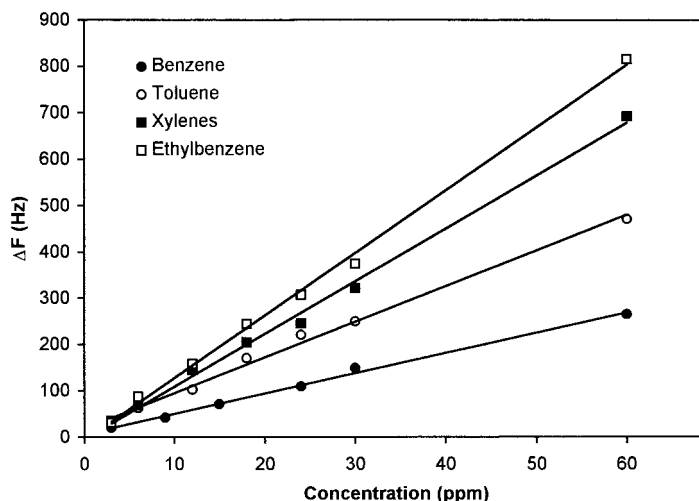
Figure 5 Calibration graphs for benzene, toluene, xylenes, and ethylbenzene. Each of responses is the frequency shift of the quartz crystal coated PDMS during exposure to the various concentrations of each of compound's vapors.

mass sensitivity) was not high enough for detection (Fig. 3). Therefore, the films obtained with the 0.5% PDMS solution, of approximately 500-nm thickness, was considered as optimum in all the sensing studies.

The polymer-coated crystal (by 0.5% PDMS solution) was exposed to a constant concentration of BTEX compounds (15 ppm). The frequency shifts after a period of 40 min for benzene, toluene, xylene, and ethylbenzene were 72, 135, 176, and 196 Hz, respectively (Fig. 4). The differences in the value of the frequency shift can be related to their partition coefficient between PDMS and the gas phase.[22,23] As previously described, the affinity of xylenes and ethylbenzene for the adsorbent of PDMS is more than that for benzene and toluene.[22,23]

To determine each compound, a calibration graph was constructed by plotting the frequency change against to the various concentrations of each organic compound (Fig. 5). According to the calibration graphs, the concentration of the BTEX compound can be determined in the range of 3–60 ppm. Characteristic parameters including correlation coefficients, limits of detection, sensitivity factors, and relative standard deviations were calculated and are presented in Table I.

The limits of detection (LOD) were calculated from calibration graphs according to the method described by Miller and Miller.[24] The detection limits for all the compounds were at levels of 1.5 ppm (Table I). The sensitivity factors, defined as the slopes of the plots of the frequency change against the concentration, indicated that the or-

ders of sensitivity are as follows: ethylbenzene, xylenes, toluene, and benzene (Table I). This can be related to the different affinities of the compounds for the adsorbent of PDMS, in agreement with the previous observations.[21,22]

CONCLUSIONS

In conclusion, a piezoelectric crystal coated with a thin layer of PDMS was developed as a sorption detector for the low concentrations of BTEX compounds vapors. It can be seen that the frequency changes increased gradually with increasing concentrations of the compounds and good linear relationships could be obtained in the concentration ranges of 3–60 ppm.

Table I Characteristic Parameters of the Determination of BTEX Compounds by Polymer-coated QCM

Compound	R^{2a}	Sensitivity Factor (Hz/ppm)	LOD[b] (ppm)	RSD % ($n = 5$)
Benzene	0.996	4.37	1.4	9.3
Toluene	0.994	7.72	2.1	7.6
Xylenes	0.995	11.40	1.2	2.6
Ethylbenzene	0.996	13.54	1.4	6.5

[a] Square correlation coefficient.
[b] Limit of detection (signal-to-noise ratio = 3).

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