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Response of Two Coated Piezoelectric Sensor Polymers to Toxic Compounds.

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ABSTRACT

The purpose of this study is to realize a device capable to detect a toxic vapor chemical substance. The polymers are coated, by drop-coating method on a 10MHz quartz crystal microbalance (QCM) to investigate their gas sensitive properties to the toxic solvents of an ordinary laboratory. A new oscillator circuit was used. The tests were carried out in 200ml homemade chamber test. The data were transferred into a PC via a sound cable. The signal was divided with a divisor to audio frequencies. This audio signal is connected to the soundcard of the PC and we measure the audio frequency. The system gave a good response in term of reproducibility.
Keywords: sensor, polymer, quartz, oscillator.

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INTRODUCTION

Chemical toxic substances such as ordinary laboratory solvents, Chemical warfare agents (CWA) and Organophosphate compounds (Ops) are significant environmental pollutants because of their widespread use. The detection of these chemical hazardous seems very important. Many methods in this purpose are used.

Traditionally, the most frequently used methods are gas chromatography [1,2], liquid chromatography [3], atomic emission detection [4], gas chromatography-mass spectrometry coupled method [5] and ion chromatography [6]. However, these techniques require expensive instrumentation and highly trained personnel, as well as time consuming and unsuitable for field analysis.

To meet the demand for on-site monitoring of toxic compounds, the detectors have to be robust, portable, fast-acting, cheap, simple to operate, and they have to be very sensitive and selective to the detected vapors. Ion mobility spectrometry, surface acoustic wave (SAW) sensor, microcantilever piezoresistive sensor, fluorescent sensor, metal oxide sensor are promising techniques. They have been intensely studied in recent years [7].

Among the various types of gas sensors investigated, surface wave acoustic (SAW) sensors and quartz crystal microbalance (QCM) sensors have generated considerable interest due to their simplicity, ease of use and high sensitivity and selectivity. Quartz crystal microbalance (QCM) represents a high-sensitivity sensor for detection of chemical substances, and is widely utilized as a result of its robust nature, availability and affordable interface electronics [8]. The QCM sensor comprise of thin sorbent layers of a chemically selective material to collect and concentrate analyte of interest. Collection of analyte increases the mass of the sensor, resulting in a change in resonant frequency [9].

To date, many sensitive polymers for nerve agents detection have been synthesized, including poly(styrene-co-vinyl benzyl hexafluorodimethyl carbinol) [10], fluoropolyol [11], hybrid organic/inorganic polymers [12] and functionalized polysiloxane [13,14].

EXPERIMENTAL

Reagents and instrumentations

Polyaniline was chemically synthesized in laboratory. Molar ratio (oxidant / aniline) <1.15. Aniline was purchased from Merck Worldwide Company (99.5%), ammonium persulfate was purchased from Panreac Appli. Chem. (99%), HCl and methanol were purchased from Fluka Analytical (>36.5 and 99% respectively). Functionalized polysiloxane was purchased from Altech Associates. The polymers were characterized with SHIMADZU type 8400S FT-IR apparatus and with NETZSCH type 204-F1 DSC apparatus. Bi-distilled water was prepared in laboratory. Ammonia and benzene were purchased from Sigma-Aldrich Company.

Oscillator realization

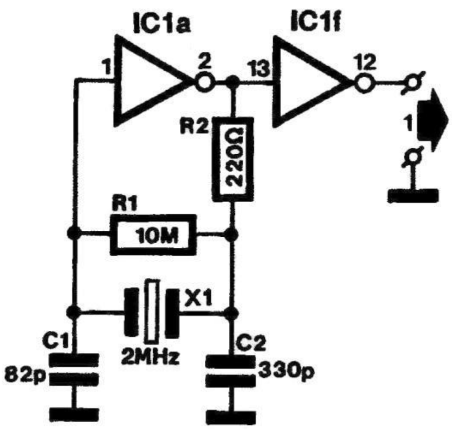

Figure 1: Oscillator circuit.

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The oscillator must give the signal the more stable. Many electronic circuits had been tested. The image below shows the chosen oscillator.

It should be noticed that the values of the capacitors (c1 and c2) must be calculated according to the initial frequency of the quartz.

RESULTS AND DISCUSSION

Sensitivity materials

The synthetic polyaniline was characterized with FT-IR and showed almost all the characterizing bonds. The table below assembles them:

Table 1: Characterizing bonds of polyaniline.

Wavenumber (cm^{-1})	Vibration mode
3447	stretching vibration of N-H bond
1561-1638	stretching vibration of C=N and C=C bonds
1409-1472	Stretching vibration of the C-C
1251-1298	Stretching vibration of the C-N bond of the aromatic secondary amine
1109	deformation vibration of the aromatic C-H bond
584-667	deformation vibration of the C-C bond

The commercialized polysiloxane OV-17 was characterized with FT-IR and showed almost all the characterizing bonds. The table below assembles them:

Table 2: Characterizing bonds of functionalized polysiloxane.

Wavenumber (cm^{-1})	Vibration mode
1260	symmetric deformation vibration (Si-CH3)
1425 – 1430	stretching vibrations (Si-phenyl)
1020 – 1191	asymmetric valence vibrations (Si-O-Si)
787	swaying methyl and stretching vibrations (Si-C)

The differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) of both polymers were realized too, and it confirmed the essence of the polymers.

Polymers coating

A small amount of polymers were dissolved, the polyaniline in dichloro acetic acid, and the phenylpolysiloxane in the water , and the solution was subsequently added dropwise onto the center of the QCM electrode by a 125µL microsyringe. The coated QCM was then baked at 50 ◦C for 0.5 h to obtain stable films. After the solvent had evaporated, a solid film was deposited on the electrode surface. The testing gases were then injected into the chamber, and the resonant frequencies of the QCM sensors were recorded.

Oscillator test

Preliminary tests for the electronic circuit (oscillator) were carried out to ensure its efficiency. The figures below show the displayed results on a of 6 decimal places accuracy frequency meter.

The screen shows that the 10MHz tested quartz gave very acceptable results in terms of precision and stability.

Figure 2: Displayed frequencies of 10MHz quartz oscillator

Sensor response and linearity

The first tests were carried out qualitatively using the polyaniline with ammonia, benzene, pyridine, paraldehyde and xylene. The results showed a good reproducibility with some difference. This, may be referred to the static mode of injection using a gas syringe which. Figures below show these results.

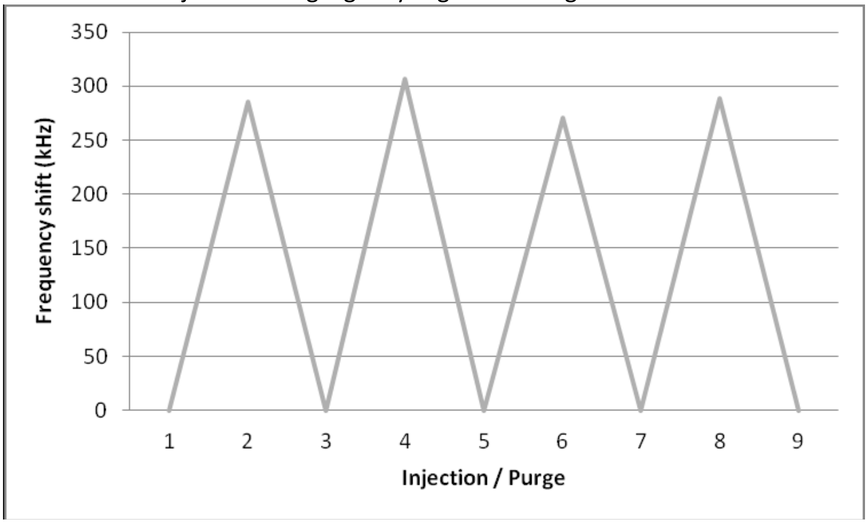

Figure 3: Variation of frequency shift depending to the polymer coated quantity

It's obvious that the frequency value of the quartz decreases with the increasing of the quantity of the polymer deposited on the crystal, that's due to the weight of the polymeric solution which load the vibration of the crystal.

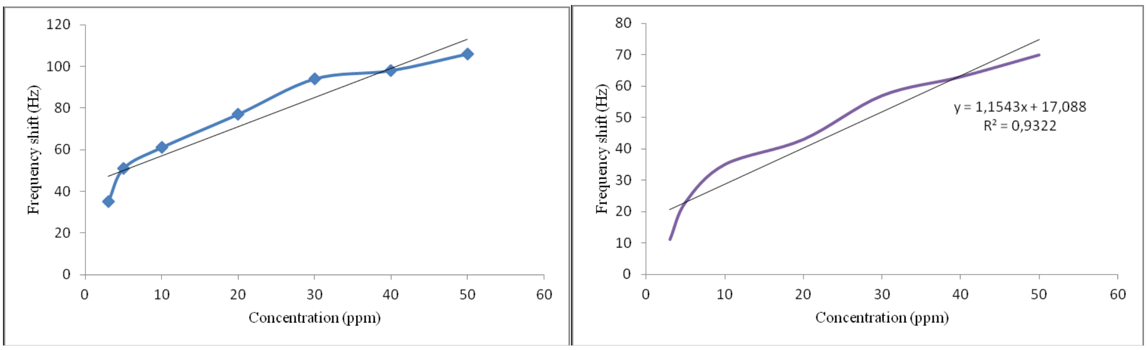

Figure 4: Linearity response in range of 3 – 50ppm (a) Water; (b) benzene

The sensor shows a good linearity with the solvents in a range of 3 – 50ppm. From the curves shown in figure (Fig. 4.), its very clear that the polysiloxane functionalized has a good linearity response to the different tested solvents, and it has a particular response with the humidity. The benzene showed the lowest slope.

CONCLUSION

Two polymers were coated on 10MHz quartz crystal, the polyaniline and the phenylpolysiloxane. The sensor responses correctly and showed a good linearity to humidity and benzene. Many calculations must be done for more results. The anomaly of this work is the handling with small amounts in wide of ppm. The work is promising and can be improved subsequently.

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