



A polymer-Metglas sensor used to detect volatile organic compounds

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ABSTRACT

In this work, the commercial polymer BAYHYDROL-110 has been employed as the analyte-responsive recognition layer on a magnetoelastic sensor used to detect several volatile organic compounds. The sensor exhibits enhanced selectivity to o-xylene and p-xylene compared to six other tested volatile organic compounds as well as to humidity. The sensitivities to o-xylene and p-xylene were -0.27 and -0.19 kHz/ppm of vapor concentration in air, respectively. The sensor exhibits excellent repeatability and stability over a period of at least 75 days, and relatively quick response times (on the order of a minute), but rather low recovery times (in the range of several minutes). The sensor's sensitivity increases linearly with the mass of the polymer, but it is only slightly dependent on the sensor's length.

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1. Introduction

Volatile organic compounds (VOCs) are organic liquids with high vapor pressure. They are frequently found in air as a result of both human activities (i.e. exhausts, industrial processes) and natural sources (i.e. deciduous trees). Unfortunately, many VOCs are hazardous and are known to cause long-term health and environmental problems even down to the ppm concentration ranges, making their detection a necessity [1–3]. Of special interest are low-cost, low-power and portable detection techniques. Numerous VOC detection techniques have been proposed in the literature, based on different principles such as quartz-crystal-microbalances (QCM) [4–7], surface-acoustic-wave (SAW) [8,9] sensors, microcantilevers [10,11], resistive [12,13] and optical sensors [14,15]. One common feature of these techniques is an appropriate coating which is used as a sensitizing layer. Its role is to selectively adsorb VOCs, which result in a corresponding shift in the sensor detection property such as resonance frequency, resistance, refractive index, etc. Commonly used materials for sensitizing layers are semiconducting metal-oxides [16,17] and conductive polymers [18,19]. However, these materials frequently have limited selectivity, require high operational temperatures (200–500 °C), or have issues related to long-term stability. In the current work, a commercially available polymer, BAYHYDROL-110 (an anionic

dispersion of an aliphatic polyester urethane resin in water/n-methyl-2-pyrrolidone), is used as the adsorbing layer together with a magnetoelastic sensor. This particular polymer has been used by other groups [20] as a protective layer on magnetoelastic sensors, but we discovered that it is also an excellent adsorbing layer for various VOCs.

Throughout the past decade there has been considerable interest in magnetoelastic sensors due to their low cost and remote query ability [21–25]. Magnetoelastic materials are usually amorphous metallic alloys, commonly known as Metglas, or composites of rare-earth elements, such as Terfenol. Our magnetoelastic sensor consists of a strip of Metglas 2826MBA with an average composition of $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$, which can be set to resonate under an external alternating magnetic field. The vibrations result in the generation of both acoustic and magnetic flux, which can be detected by an appropriate microphone or a pickup coil. The measured flux passes through a maximum when the strip is vibrating at its resonance frequency f_0 , given by [26]

$$f_0 = \frac{1}{2L} \sqrt{\frac{E}{\rho_s(1-\nu^2)}} \quad (1)$$

where E , ρ_s , and ν are correspondingly the Young's modulus of elasticity, the density, and the Poisson's ratio of the Metglas material, and L is the length of the strip. The Poisson ratio is defined as the ratio of the lateral strain (normal to the applied load) to the axial strain [27]. Usually the $(1-\nu^2)^{-1/2}$ term is ignored for simplicity because it only amounts to approximately a 3% correction to f_0 for typical values of $\nu = 0.25$. Starting with Eq. (1) it can be easily shown

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that when a sensor of mass m_0 and resonance frequency f_0 is uniformly loaded by some small mass Δm , the resulting shift of the resonance frequency Δf is given approximately by:

$$\Delta f \approx -f_0 \frac{\Delta m}{2m_0} \quad (2)$$

Based on this principle, different physical and chemical parameters can be measured by coating the sensor with an appropriate mass change, analyte-responsive recognition layer which is capable of selectively adsorbing certain molecules. In this way various parameters have been previously detected such as CO₂ concentration [28], humidity [29], bio-salts like calcium oxalate and brushite [30], pH [31], glucose [20], and microorganisms [32,33]. The advantages of using magnetoelastic sensors are (a) the remote sensing by means of pick-up coils, (b) the sensor's low price which can be used on a disposable basis, and (c) the low power and cost of the equipment. Further information concerning the principles of operation, as well as the design and applications of magnetoelastic sensors [34–37], can be found in the review of Grimes et al. [21] and in the references mentioned therein.

In the current work, we present the ability of the BAYHYDROL-110-Metglas sensor to detect various VOCs at different concentrations in synthetic air at room temperature. Eight different VOCs were examined for that purpose, with compositions varied between 0.05% and 11% depending on the examined VOC. Experiments with humidity were also carried out since it is a basic ingredient of the atmosphere and tends to interfere with the sensor's signal. This new sensor can selectively detect *o*-xylene and *p*-xylene compared to other VOC's (*n*-hexane, *c*-hexane) and humidity.

2. Materials and methods

The commercially available polymer BAYHYDROL-110 was used throughout this work. This polymer has been used by other authors in the literature [33–38] as a protective layer of the magnetoelastic ribbons due to its excellent binding properties to the metallic glass surfaces and its long-term stability in aqueous environments where most of the polymers fail. We discovered that BAYHYDROL-110 shows a very positive response to several VOCs, with various sensitivities. The polymer was spread on the outer surface of 2 mm × 6 mm × 28 μm Metglas 2826 MBA magnetoelastic strips using a glass spatula. The response of the sensor was tested for the following eight different VOC's: *c*-hexane and *n*-hexane, benzene, *o*-xylene and *p*-xylene, ethyl-acetate, methyl-ethyl-ketone (MEK) and dichloromethane. The experimental setup used for the detection of the VOCs is shown in Fig. 1. The concentration of each VOC was controlled using the following procedure: a stream of synthetic air was fed to a saturator (bubbler) with the VOC of interest. The concentration of the VOC was adjusted by diluting it with a second stream of synthetic air. The VOC vapor concentration was calculated assuming that the air stream leaving the bubbler was saturated with organic vapors and by taking into account the vapor pressure of each particular VOC at room temperature.

Fig. 2 shows typical sensor resonance peaks as a function of polymer mass under the flow of synthetic air. As the inset shows, the dependence of the resonance frequency f_0 on the polymer mass m is quite linear for polymer masses up to 30 mg, in accordance to Eq. (2). For the rest of the current work, all polymer masses were chosen to lie within this linear region. The adsorbed mass is typically only a small fraction of the polymer mass and thus it does not cause deviation from the linear region. The slope of the straight line is equal to 0.834 kHz/mg and it can be used as a calibration factor to convert resonance frequency shifts to mass loads.

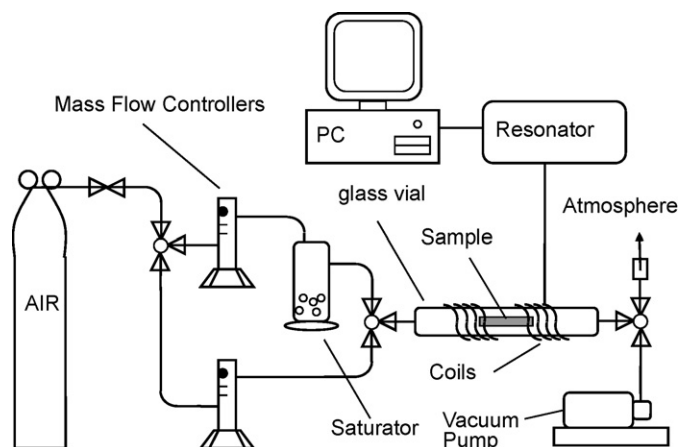


Fig. 1. Experimental setup designed to detect VOCs using a polymer-Metglas sensors.

3. Results and discussion

3.1. VOC detection

Fig. 3 shows the responses of a sensor when it is exposed to alternating environments of air and VOC at various concentrations. Measurements of humidity are also shown for comparison. All graphs are depicted on the same vertical scale. It is clear from these graphs that the sensor shows a small response to humidity, no remarkable response to either of the hexane compounds, and a remarkable response to the other VOCs with various sensitivities. Even though it is not apparent at a first glance, the sensitivity of the sensor to the xylene compounds is at least a factor of 10 higher than the other VOCs. This becomes more evident in Fig. 4a where the average stabilized resonance frequency values of Fig. 3 are depicted as a function of the VOC concentrations. The three ellipses have been drawn by the authors to stretch the fact that there are three different sensitivity ranges; a small one (range I) which includes the *n*- and *c*-hexane, a large one (range III) with the xylene isomers, and a middle one (range II) with the rest of the compounds. Humidity data, which is shown for comparison, lies in the middle range.

The sensor's sensitivity, which is defined as the signal change per concentration change, equals the slope of the data curves of Fig. 4a, assuming a linear dependence. The results for each individual VOC are shown in Fig. 4 as a selectivity plot, which clearly indicates the preference of the sensor to the xylene isomers. Table 1 also presents these sensitivities as numerical data for the three afore-

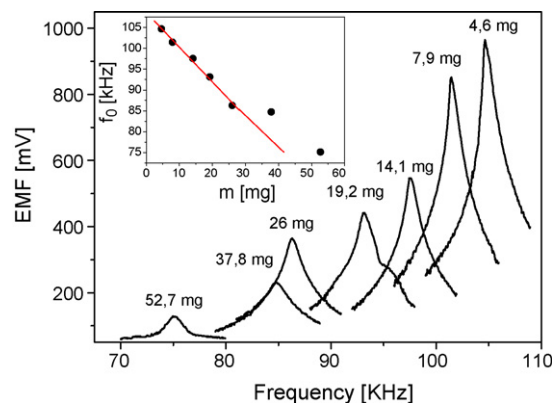


Fig. 2. Shifts of the resonance peaks as a function of polymer mass deposited on the Metglas ribbon.

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