



Enhancing detection of nitroaromatic vapors by utilizing polymer coatings on quartz crystal microbalances having strong dipoles



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ABSTRACT

A novel class of PDMS based polymers containing azobenzene side chains were synthesized and evaluated as coatings for quartz crystal microbalance (QCM) based sensors to detect nitroaromatic vapors. The polymers contain functional groups (p-substituted azobenzene moieties and hydroxyl groups) that can interact with compounds with large dipole moments such as nitroaromatic chemicals through a combination of permanent dipole-dipole interactions and hydrogen bonding. A QCM sensor array was prepared by coating different polymers onto the surface of a quartz crystal and evaluating the response of the each coating to saturated vapors of a variety of analytes such as toluene, octane, 2-nitrotoluene, nitrobenzene, and 2,4 dinitrotoluene. The incorporation of azobenzene moieties in the polymer structure increased the sensor response towards the nitroaromatic analytes. Pattern recognition techniques such as principal component analysis (PCA) and decision tree learning methods were applied to evaluate the sensor response and predict analyte identity. A classification accuracy of 96% was obtained using classification and regression trees (CART) based learning. This novel approach opens new possibilities in ultrasensitive detection of chemical vapors with significant dipole moments.

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1. Introduction

Common nitroaromatic explosives have low vapor pressures at room temperature and therefore detection of trace quantities of these compounds under ambient conditions requires extremely sensitive detection technologies [1]. Sensors based on ion-mobility spectrometry (IMS) are often used for the detection of explosives at airport security check points [2]. IMS based devices have excellent sensitivity that allows the detection of trace quantities of these explosives. However, as with other detection techniques IMS also can exhibit false positive responses [3].

IMS has been used to determine the charge to mass ratio and mobility ratios of over 22 compounds of interest to national security (including explosives, illicit drugs, and chemical warfare agents) [4]. This study indicated that chemicals present in cosmetic products (including fragrances, cosmetics, sunscreen lotions) commonly encountered in airports could potentially interfere with

detection analytes of interest (explosives, drugs, chemical warfare agents). More importantly 17 suspected contaminants found in airport settings decreased the sensitivity of TNT detection [5]. Thus, there exists the need for alternate sensing technology platforms that can be integrated with systems that are portable and low-cost to provide improved sensitivity and specificity for the detection of nitroaromatics.

The success of canines in chemical identification has motivated research in 'electronic nose' systems that attempt to mimic the canine olfactory system. Electronic nose systems usually comprise several sensing elements, each of which can detect different chemicals. The combined signals obtained from these sensors are analyzed using intelligent signal processing algorithms and complex pattern recognition tools to substantially minimize false positive responses while preserving the sensitivity of detection [6].

Arrays of fluorescent polymer sensors [7–9], metal oxide sensors [10,11], quartz crystal microbalance (QCM) and surface acoustic wave (SAW) based piezoelectric mass sensors [12] have been investigated over the past decade as possible alternatives to the already commercially available ion-mobility based sensors. QCM based sensors have been reported for the vapor phase detection

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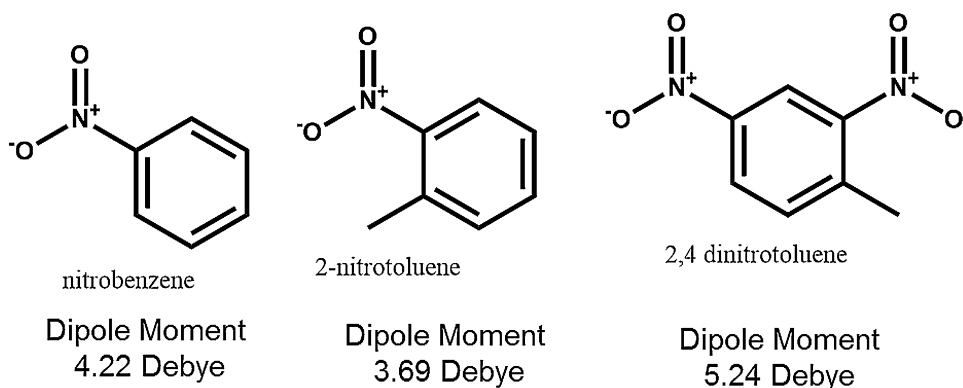


Fig. 1. Structure and dipole moments of Nitroaromatic analytes evaluated in this study.

of chemical warfare agents [13–16]. These devices have demonstrated sensitivity to various organic chemical vapors. QCM sensors are compact and are capable of being miniaturized for the on-site detection of nitro aromatic explosives and explosive precursors.

The sensitivity and selectivity of the piezoelectric mass sensors (QCM and SAW) can be enhanced by the incorporation of surface coatings [17]. The surface coating (polymers or metal oxides) that form the active layer can interact with test analytes through various mechanisms that include solvation, secondary interactions between permanent dipoles and hydrogen bonding.

Most polymer coatings designed to serve as the active layer for these sensors reported to date utilize hydrogen bonding interactions [17] to adsorb chemical analytes. Polymer coatings containing hydrogen-bond acidic moieties have been used for the detection of organo-phosphorus nerve gas simulants such dimethyl methylphosphonate (DMMP) [18,19]. Incorporation of fluorinated alcohols or fluorinated phenols (groups that exhibit strong hydrogen bond acidity) in polymers has been demonstrated to be beneficial for obtaining sensitive coatings capable of detecting chemical vapors through hydrogen bonding [20] interactions. Hexafluoroisopropanol functionalized siloxane based polymers have been synthesized and evaluated as vapor sensitive coatings for use with chemical sensors. While these strong hydrogen-bond acidic polymers have demonstrated strong affinity for nerve gas simulants, they are not very sensitive for the detection of nitroaromatics such as DNT [20].

Nitroaromatic analytes like nitrobenzene, 2-nitrotoluene (2-NT) and 2,4 dinitrotoluene (2,4 DNT) have large permanent dipole moments (in the range of 3–6 Debye) as shown in Fig. 1, and can interact with functional coatings through dipole-dipole and dipole-induced dipole interactions.

One of the strategies we have reported for improving the sensitivity in detection of analytes with high dipole moment is to utilize polymer coatings containing functional group that exhibit large dipole moments. In this regard, *p*-nitroazobenzene moieties have an electric dipole of about 4.45 D [21], while the *p*-carboxylic acid azobenzene moieties have a dipole moment of 2.9 D [22]. Thus nitroaromatic analytes could interact with the azobenzene functional groups via dipole-dipole interactions.

We have previously reported that a polymeric coating containing functional groups with strong dipole moments can indeed interact with explosive vapors. Polypropylene glycol based coatings containing *p*-nitroazobenzene moieties were synthesized and tested as active layers in QCM sensors for the detection of nitroaromatics [23].

The *p*-nitroazobenzene functionalized PPG coating (see Fig. 2) exhibited significantly higher response to saturated nitroaromatic vapors when compared to the unfunctionalized PPG coating polymer without the azobenzene moieties (see Fig. 3). Polymer coatings

used as active layers for QCM and SAW sensors must have glass transition temperatures below the operating temperature of the sensing device [17]. While the PPG containing polymers exhibited some response to nitroaromatics, there were several shortcomings in terms of reversibility of the sensor response. The polymer backbone was not as porous as desired to maximize the interactions of the azobenzene moieties with analytes of interest. PDMS offers better porosity and flexibility to improve dipole-analyte interactions, therefore improving sensitivity of detection. Polysiloxane based materials modified with aniline moieties have been evaluated as functional modifications for QCM sensors used for the detection of nitroaromatic vapors [24]. Nitroaromatic compounds such as nitrobenzene, dinitrobenzene, DNT, trinitrobenzene and trinitrotoluene were tested in this study. In these coatings, the underlying mechanism of interaction is attributed to H-bonding between the aniline groups present in the polymer and the nitro groups present on the analyte.

In order to test the hypothesis that a coating with lower glass transition temperature (T_g) and better diffusivity can indeed help with interactions of analytes with organic moieties with high dipole moment, *p*-nitroazobenzene functionalized PDMS based polymer was synthesized and tested in a Surface Acoustic Wave (SAW sensor). Preliminary studies evaluating the coating response to nitroaromatic explosive and explosive precursors indicated better sensitivity [25].

In this study, poly(dimethyl siloxane) (PDMS) based polymer coatings containing a combination of moieties that can hydrogen bond with analytes (specifically nitroaromatics) and functional groups with large dipole moment (*p*-substituted azobenzene moieties) is reported. The polymers synthesized were coated on QCM sensors and the effectiveness of the QCM sensor array in detection of trace quantities of nitroaromatic analyte vapors (2-nitrotoluene, nitrobenzene and 2,4 DNT) as well other organic analytes such as toluene, and octane was evaluated. Decision tree-based learning methods were applied to evaluate the performance of sensor array.

Decision tree-based learning methods are powerful and popular machine learning tools for classification and making numeric predictions [26]. The attractiveness of decision tree-based learning methods over other machine learning techniques such as neural networks, include their ease of use, and generation of easily inspected models with rules that can be readily understood. Models created using this method display internal nodes that form a tree-like structure (hence the name). The internal nodes (test nodes) represent tests on a feature's (variable's) values, and the leaf nodes (terminal or decision nodes) are assigned classes. Decision trees are learned by recursively selecting the variables that “best” sort the data into non-overlapping subsets. As the splitting continues, the variables chosen for splitting the data are arranged into a tree, with the first variable chosen for splitting forming the root of the

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