DEVELOPMENT OF HIGHLY SELECTIVE SINGLE SENSOR MICROFLUIDIC-
BASED GAS DETECTOR

by

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DEVELOPMENT OF HIGHLY SELECTIVE SINGLE SENSOR MICROFLUIDIC-BASED GAS DETECTOR

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Abstract

This research aims at the integration of gas sensors into microfluidics platforms to develop low-cost, portable, and highly selective (with a fast recovery time) detection tools for discrimination of volatile organic compounds (VOCs). The main advantage of the proposed device over previous microfluidic-based gas sensors is the enhanced selectivity by optimizing the microchannel geometry and implementing a novel multi-layer surface coating. These enhancements resulted in reducing the sensor recovery time to less than 150 seconds, as opposed to over 15 minutes reported in previous studies. A thorough study is also conducted to further investigate the effect of analyte polarity and the choice of channel surface material (creating different hydrophobicity) on gas discrimination. It is shown that the device segregation capability between different compounds highly depends on the target gas polarity and hydrophobicity of the channel surface material (reflecting its surface energy and interaction with the analyte). Finally, to eliminate the faulty effect of humidity on the sensor’s response, a diffusion-based humidity control membrane (made out of inorganic salts) is added to reduce and stabilize the level of relative humidity at 15%. The transient responses of the sensor in different humidity levels show that the proposed humidity control system also significantly enhances the selectivity of the device.

A range of different target analytes including alcohols, ketones, and alkanes are tested using the proposed detector. The results show that the device can successfully differentiate between different gases (and even gas mixtures) at small concentrations (at the ppm level), showing the diagnostic power of the developed sensors. The device is then tested for wide range of applications including: 1) identification of wine samples for which different types of wines from different manufacturers and vintage years are differentiated; 2) monitoring tetrahydrocannabinol (THC) in air samples for potentially detecting the cannabis use; and 3) leakage detection along the pipeline in which the device was used for identifying pentane traces in a field test. This wide range of applications shows the power and versatility of the proposed gas detector technology.
Preface

The research presented in this thesis is the original work performed by the author. This thesis was supervised by Dr. Mina Hoorfar at the Advanced Thermo-Fluidic Laboratory (ATFL) in the School of Engineering, University of British Columbia. Parts of this thesis have been published in different journals and presented in conferences. The details of the publications and the author’s contributions in them are explained below:

a. Book chapter

b. Refereed journal publications


c. Conference proceedings and presentations


d. Patent

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-nose</td>
<td>Electronic nose</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>S</td>
<td>Sensitivity</td>
</tr>
<tr>
<td>ppm</td>
<td>Part per million</td>
</tr>
<tr>
<td>$R_{air}$</td>
<td>Resistance of the sensor in the clean air</td>
</tr>
<tr>
<td>$R_{gas}$</td>
<td>Resistance of the sensor in the exposure to a target gas</td>
</tr>
<tr>
<td>$G_{air}$</td>
<td>Conductance of the sensor in the clean air</td>
</tr>
<tr>
<td>$G_{gas}$</td>
<td>Conductance of the sensor in the exposure to a target gas</td>
</tr>
<tr>
<td>$V_b$</td>
<td>Bias voltage for the sensor</td>
</tr>
<tr>
<td>$V_h$</td>
<td>Bias voltage for the heater</td>
</tr>
<tr>
<td>$Sel(i,j)$</td>
<td>Selectivity between gas $i$ and gas $j$</td>
</tr>
<tr>
<td>MOS</td>
<td>Metal oxide semiconductor</td>
</tr>
<tr>
<td>$C(x,t)$</td>
<td>Concentration of gas molecules along $x$ axis in different times</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient (diffusivity) in air</td>
</tr>
<tr>
<td>$C_s$</td>
<td>Concentration of gas molecules adsorbed to the channel surface</td>
</tr>
<tr>
<td>$C_a$</td>
<td>Surface density of adsorption sites</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>Fractional surface coverage</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Modified Longmuir coefficient</td>
</tr>
<tr>
<td>$l$</td>
<td>Channel length</td>
</tr>
<tr>
<td>$W$</td>
<td>Channel width</td>
</tr>
<tr>
<td>$d$</td>
<td>Channel depth</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Initial concentration of target gas in the chamber</td>
</tr>
<tr>
<td>$t_e$</td>
<td>Exposure time</td>
</tr>
<tr>
<td>$G_n(t)$</td>
<td>Normalized response</td>
</tr>
</tbody>
</table>
\( t_r \)  
The time at which the normalized response level reaches 5 \%

\( t_m \)  
The time at which the normalized response level reaches 95 \%

\( R_f \)  
Final readout of the normalized response

\( CVD \)  
Chemical vapor deposition

\( PMMA \)  
Polymethyl methacrylate

\( F_1 \)  
Signal maximum response level

\( F_2 \)  
Response level for the final readout

\( F_3 \)  
Area underneath the response curve

\( \varnothing \)  
Feature vector

\( \theta \)  
Contact angle

\( \gamma_{LV}^d \)  
Dispersive liquid-vapor surface tension

\( \gamma_{LV}^p \)  
Polar liquid-vapor surface tension

\( \gamma_{LV} \)  
Liquid-vapor surface tension

\( \gamma_{SL} \)  
Solid-liquid surface tension

\( \gamma_{SV}^d \)  
Dispersive Solid-vapor surface tension

\( \gamma_{SV}^p \)  
Polar Solid-vapor surface tension

\( \gamma_{SV} \)  
Solid-vapor surface tension

\( KOH \)  
Potassium hydroxide

\( MgCl_2 \)  
Magnesium chloride

\( NaBr \)  
Sodium bromide

\( NaCl \)  
Sodium chloride

\( K_2SO_4 \)  
Potassium sulfate

\( DMF \)  
Digital Microfluidics
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In the first place, I would like to express my gratitude to my supervisor Dr. Mina Hoorfar for her great guidance and supervision during my PhD career. She has always been a great role model and source of inspiration to me.

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I am very thankful to all of my friends and colleagues who shared part of their lives with me and created unforgettable memories.

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Dedication

This thesis is dedicated to my parents and my brother (Ali) for their endless love and support.
Chapter 1 Background

1.1 Introduction

The olfaction system [1-2] or sense of smell is one of the most important human (and animal) abilities. There have always been interests and efforts in developing devices that can mimic animals and human olfaction systems (similar to other sensory devices like machine vision [3], machine hearing [4], machine speaking [5], and electronic tongue [6]). Macro and micro olfaction machines have been developed over the past century [7]. The state-of-the-art technology available in the industry today for real-time gas detection is the electronic nose or e-nose (similar to human olfactory system) which functions based on sensor arrays coupled with pattern recognition systems [8-12]. Such systems provide a fingerprint response to a given odor which is then identified and discriminated using pattern recognition software [10].

In this chapter, first the human olfaction system (and how it functions) is introduced. Then, different micro and macro systems developed based on machine olfaction are briefly mentioned. The operation principles of e-nose systems are then discussed. Also, the newest e-nose technologies available for different applications are introduced.

1.2 Odor and sense of smell

Odor is a sensation generated when odorant (gas) molecules interact with receptors in the olfactory neurons in the (human) nose which can sense more than 10000 different odors [13-14]. Despite our intuitive sense of smell, the operation principle of smelling was not revealed before 1991; Linda Buck and Richard Axel discovered a family of multigenes which encode the olfactory receptors in human nose. This significant discovery resulted in winning the Nobel Prize in physiology and medicine in 2004 for Buck and Axel [15].

Our nose affects the quality of our life significantly: detection of toxic gases in the environment, fire awareness, identifying spoiled food, good feelings initiated by pleasant smells, and memories triggered by different scents are among numerous examples. Different parts of human olfaction (which is near by the vision systems) and their connections to the brain is shown in Figure 1-1. The nose is the only external part of our olfaction system. The odorant molecules enter through the nasal cavity and reach the olfactory receptors which are placed between our eyes [16]. The receptor neurons are connected to the olfactory bulb which is part of our brain. The olfactory bulb is connected to the olfactory cortex which is in charge of signal analysis and pattern recognition of different smells. While the air goes
through the nasal cavity, the temperature of the air reaches the temperature of body. In the presence of any odorant in the air, the molecules of the odorant react with the olfactory receptors and that results into the sense of smell [13-14]. In the literature, it is emphasized that there is a difference between the sense of smell and sniffing the smell. Sniffing is mentioned to be a part of smell detection [17].

![Figure 1-1](image.png)

**Figure 1-1** Different parts of olfaction system and their connections to brain (Reproduced from [16] with permission from Elsevier).

In essence, the olfactory receptors are the main part of the smelling process since they produce the electrical pulse which is transferred through the olfactory bulb to the neurons and hence the brain for signal analysis and pattern recognition. Similar to other senses which work based on the receptor cells in our body that convert environmental stimuli to an electrochemical pulses (e.g., our vision receptors response to electromagnetic signals which are received by the cornea in our eyes; sense of hearing is based on the reactions of neuron receptors in our ear towards sound wave; and tongue provides chemical understanding from the surrounding environment), olfactory receptors are neuron cells which are placed in epithelium [18-19]. There are more than 10 million olfactory receptor cells in epithelium which has a surface area of 2-4 cm² [20]. Epithelium is covered with a 10-40 μm thick layer
of mucus. The gas molecules are adsorbed to this layer, diffuse into, and reach the olfactory receptors. The schematic and image of the olfactory receptor system is shown in Figure 1-2. The end of each cell reaches the surface of the epithelium through tiny hairs which are called cilia [21-22]. Each cell has 10-20 cilia which are 160-µm long at their maximum length. G-protein-coupled receptors (GPCR), which are receptors for gas molecules, are dispersed on the surface of these cilia [23]. Each olfactory receptor responds only to certain gas molecules. Therefore, by exposing the olfactory system to a chemical compound, some of the olfactory receptors get activated and the rest are deactivated. In essence, if there are “n” receptors and each has two modes (active and non-active), “2ⁿ” scenarios might occur. This results in encoding different smells in the olfactory system. In the next section, different technologies developed to mimic the above process are presented [24-25].

Figure 1-2 (A) SEM image of olfaction receptors. (B) Schematic of olfactory receptor system and different parts of it (Reproduced from [21] with permission from Nature Publishing Group).
1.3 Machine olfaction

Rapid, sensitive and high precision artificial olfaction devices are in demand for gas analysis for different applications including beverage and food quality assessment [26], analytical chemistry [27], biological diagnosis [28-30], and safety and environmental monitoring [31]. Numerous methods have been proposed for detecting gases in particular volatile organic compounds (VOCs). Gas chromatography (GC) and mass spectrometry (MS) are the most commonly used “macro” systems developed for the analysis of VOCs [32-33]. Although GC and MS have high accuracy and reliability, these methods are expensive and time consuming, and require bulky devices and highly skilled personnel to run them. Also, the sample extraction and experimental processes involved using these methods are sophisticated and time consuming. Recent efforts have focused on miniaturizing these devices to enhance their processing time and reduce the required sample volume [34-35]. Due to the complexity of their operational principles and their dependency on sophisticated accessories, the miniaturization of systems such as gas chromatography and mass spectrometry in a low-cost fashion has not been realized yet [36].

To address the shortcomings of these conventional devices, electronic noses (e-nose) have been developed as an alternative method for gas detection. Although GC and MS provide quantitative and qualitative data for single gas and gas mixture analysis, these methods are not called “e-nose” as their operation principle is not similar to the biological model (human or animal nose). Here the basic principles of each of these methods are discussed.

1.3.1 Gas Chromatography (GC)

A gas chromatograph (GC) is an analytical instrument that measures the content of a mixture of different gas components in a sample (see Figure 1-3). During the gas chromatography process, the sample injected into the instrument is transported by a stream of gas (referred to as the “carrier gas”) into a separation channel known as the “column” [37-38]. Helium or nitrogen is used as the carrier gas. Different components are then separated along the column. The detector placed at the end of the column measures the quantity of the components that exit the column. To measure a sample with an unknown concentration, a standard sample with known concentration is injected into the machine. The standard sample peak retention time (appearance time) and the magnitude of the peak are compared to the test sample to calculate the concentration of the unknown sample [39].
The separation of different components in a gas mixture occurs along the column due to interaction of two different phases of the material: mobile phase and stationary phase. The mobile phase is due to the carrier gas which moves along the column. The stationary phase is because of the oily non-volatile coating inside the column. The traveling time (retention time) along the column is dependent on the polarity and molecular weight of the components. Different components travel along the column with different speeds and therefore different time which results in separating the gas components.

### 1.3.2 Mass Spectrometry (MS)

MS is another “macro” system used for identification of different compounds of a gas mixture. The sensitivity and selectivity of this method is high, and it is usually used in series with a GC to identify different compounds of components in a gas mixture [40]. The most important parts of a MS system are: a ionization source in which the sample is ionized, a mass spectrometer in which the components are separated based on their mass per charge ratio using a strong magnetic force, and a detection unit in which the separated ions are identified and recorded in a computer. The schematic of different parts of MS are shown in Figure 1-4 [41].
1.3.3 **Electronic nose (e-nose)**

An artificial nose sensor, also called “electronic nose” (e-nose), has been developed to mimic the human nose. E-noses operate based on sensor arrays coupled with pattern recognition systems [42]. As for the sensory part of the e-noses, an array of several sensors (including optical, colorimetric, and piezoelectric based sensors) are used [10]. The idea of e-noses for gas detection was first suggested in 1980 in Argonne National Laboratory near Chicago, IL [43]. The goal was to develop a portable device (to be carried on transportation trucks, trains, and ships) for detection of flammable gases. Dr. Stetter was the technical lead of this project. In 1984, this project succeeded and resulted in a device called “CPS-100”. This e-nose was the first portable version of e-nose which was used for monitoring the hazardous chemicals. The picture of this device and the group of researchers involved in this project are shown in Figure 1-5 [43-44]. The history of electronic nose, however, dates back to 1961 (even before CPS-100 was made). Different stages of growing path of this technology are shown in Figure 1-6 [45].

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**Figure 1-4** The schematic of different parts of mass spectrometry (MS) (Reproduced from [41] with permission from Springer).
Figure 1-5 (A) The team of creators of the first electronic nose; from left to right: S. Zaromb, M. Findlay, W. R. Penrose, J. R. Stetter. (B) The first version of the electronic nose (Reproduced from [43] with permission from Encyclopedia).

Figure 1-6 The history of electronic nose until 2009.

- 2009 Cyber nose
- 2008 3rd generation of JPL eNose installed for STS-126 Mission
- 1998 Nose on a Chip Idea
- 1995 First commercial modular system (Lennartz Electronic, metal oxide sensors, QMBs, calorimetric sensors)
- 1993 First commercial nose (Odor Mapper Ltd., conducting polymers)
- 1990 First Specific seminar on Electronic Nose
- 1987 Name “Electronic Nose”
- 1985 Ikegami (sensor array, conductivity sensors)
- 1984 Stetter (CPS-100, Electrochemical sensors)
- 1982 Persaud, Dodd (sensor array, metal oxide sensors)
- 1970 Taguchi (patents SnO2 Sensors)
- 1965 Heiland (Tin Dioxide Sensors)
- 1965 Buck (Electrochemical Sensors)
- 1964 Wilkens, Hatman (Redox Sensors)
- 1962 Seiyama (Tin Dioxide Sensors, Fundamentals)
- 1961 Moncrief (Mechanical Nose)
The name of the e-nose is chosen because of its similarity to the human nose. Different parts of the smell detection process with the human nose are shown in Figure 1-7 [46-48]. Five stages of smell detection using the human olfaction system are as follow:

1. Sniffing the smell during which the odorant molecules are adsorbed to receptor cells and stimulate them;
2. Stimulation of the olfactory receptors and producing an electrical pulse;
3. Transferring the electrical signal to mitral cells through glomerulus, which is part of the olfactory bulb;
4. Sending the neuron signals to the brain through the mitral cells; and
5. Performing signal analysis and pattern recognition in the brain, resulting in smell detection.

Figure 1-7 Different stages of smell detection in the human olfaction system (Reproduced from [48] with permission from Elsevier).
The schematic of different parts of an electronic nose is depicted in Figure 1-8 [49]. Five components of smell detection using an e-nose is as follow:

1. Sample extraction and delivering the gas molecules to the chamber where the sensor array is located;
2. Reaction of the gas molecules with the sensor sensing pallet, resulting in electrical signals;
3. Amplification and recording of the electrical signals using interface circuit;
4. Converting the recorded signals to digital data that is fed to a computer; and
5. Analyzing the data, extracting the features from the signals, and recognizing the pattern of each signal (using different pattern recognition techniques), resulting in smell detection.

**Figure 1-8** Schematic of different parts of an e-nose (Reproduced from [49] with permission from Elsevier).
The components in different stages of smell detection using e-nose devices are shown in Figure 1-9 [50]. The analyte is extracted in the chamber where the conditions of the sample (including humidity and temperature) are controlled. The sensor array is then exposed to the analyte and the electrical signals are recorded using an interface circuit and sent to a computer for data analysis. If the components of the sensor array are correctly chosen, the responses of the different sensors to the analyte are different which results in a general fingerprint for the examined sample [51]. As an example, the responses of four sensors (in an array) to three different sample gases are shown in Figure 1-10. The maximum level of the transient response is extracted and shown from each response as their features [52-53].

1.3.3.1 Sensors in e-nose

Gas sensors are devices which perform based on changing one or a few of their physical characteristics (such as mass, conductivity or capacitance) when they are exposed to a gas. Converting these changes to electrical signals results in producing the response of the sensor to different gases [54]. Different types of gas sensors are shown in Figure 1-11 [55]. The four main categories of gas sensors are optical, thermal, electrochemical, and gravimetric listed in Figure 1-11. Gas sensors are evaluated based on their performance indicators which are as follows [56]:

**Sensitivity**: the change in the measured signal of the gas sensor per analyte concentration unit which shows how precise the sensor can detect the target gas.

**Detection limit**: The minimum volume concentration of the target gas which can be detected by the gas sensor, showing how sensitive is the sensor. It is also called resolution and is defined under a given condition, particularly temperature and humidity.

**Selectivity**: The ability of the gas sensor to distinguish between different components of a mixture and detect a single specific gas.

**Response time**: the time which is required for the sensor to create a signal from reaction to a specific concentration of the target gas and recovery to its original base-line.

**Recovery time**: the time which takes for the sensor response to return to its baseline

**Power consumption**: The power dissipated by the sensor heater and sensing pallet.

**Dynamic range**: the difference between the maximum concentration of the gas that could be detected (while saturating the sensing layer surface) and the minimum detection limit.
**Life cycle**: the period of time during which a sensor can operate without stopping.

**Drift**: the gradual change in the sensing capability of a gas sensor over time which is caused by the change in the physical or chemical properties of the sensing pallet.

**Figure 1-9** Different components of an e-nose (Reproduced from [50] with permission from Encyclopedia).

**Figure 1-10** Sensor array responses and simple feature extraction of an e-nose system (Reproduced from [43] with permission from Encyclopedia).
The most frequently used type of gas sensors is metal oxide semiconductor (MOS) [57-58]. MOS sensors which were introduced by Taguchi and Seiyama [59] for the first time. In the basic configuration of MOS sensors, which is shown in Figure 1-12A, a chemoresistor is made by deposition of a thick film metal oxide pallet and a thick film thermoresistor microheater on the opposite surfaces of a millimeter-scale ceramic substrate.

The electrical behavior of a MOS sensor in a DC bias can be modeled as a variable resistance $R_s$ (see Figure 1-12B). The value of this resistance depends on the type of the gas molecule, the gas concentration, and the temperature of the sensing pallet [60]. The resistance of the sensor in the clean air is $R_{air}$ (baseline). The sensitivity ($S$) of such a sensor is defined by:

$$S = \frac{R_{air}}{R_{gas}}$$

in which $R_{air}$ and $R_{gas}$ are the resistances of the sensing pallet measured in the clean and contaminated air, respectively (see Figure 1-12C). The sensing mechanism (inter-grain potential barrier) in the absence of the target gas and in the presence of the target gas are shown in Figure 1-12D and E, respectively. As an example, the reaction between CO and the sensing pallet of the sensor is shown in Figure 1-12F [60].

**Figure 1-11** Different types of gas sensors (Reproduced from [55] with permission from Springer).
Figure 1-12 (A) The schematic of a MOS gas sensor and its bias circuit. (B) Equivalent electrical circuit of the sensor in a DC bias ($V_b$ is the bias voltage for the sensor, $V_h$ is the voltage across the heater). (C) Typical response of a sensor exposed to a certain concentration of a gas, $G_{air}$ and $G_{gas}$ are the conductance of the sensor in clean air and after exposure to a gas, respectively. (D) Model of the inter-grain potential barrier in the absence of the target gas. (E) Model of the inter-grain potential barrier in the presence of the target gas. (F) The reaction between $CO$ as a reducing agent and sensing pallet of the sensor (Reproduced from [60] with permission from Elsevier).

$$1/2O_2 + (SnO_{2-x})^+ \rightarrow O^- ad(SnO_{2-x})$$

$$CO + O^- ad(SnO_{2-x}) \rightarrow CO_2 + (SnO_{2-x})^+$$
The selectivity of a sensor between two gases \((i,j)\) is defined by:

\[
\text{Sel}(i, j) = \frac{S_i}{S_j}
\]  

(2)

in which \(S_i\) and \(S_j\) represent sensitivity of the gas sensor to the gas \(i\) and \(j\), respectively.

Current gas sensors are either made to be evenly sensitive to different gases or fabricated for detecting a specific target. Hence, differentiating among different gases or a mixture of gases using a single sensor is very challenging, if not impossible, as the transient responses of the sensor to two different gases are almost the same [60].

In a sensor array, using a few sensors at the same time provides more information related to the nature of the gas. The components of an array can be from the same or different categories of gas sensors. The number of sensors in an array is usually between 4 to 32. Recently, even a higher number of sensors in arrays are reported [61-63].

1.3.3.2 Feature extraction methods

The process of extracting information from the responses of the sensor components of an array of sensors is called feature extraction. The goal is to relate the extracted features from the responses to the type, concentration or a characteristic of the examined gas. The schematic of different stages of feature extraction is shown in Figure 1-13 [64-66]. First, the responses of the sensor are normalized and the features are extracted. In the next stage, the dimensions of the data are reduced and shown in a 2D or 3D map (called feature space [67]) for better presentation.

![Figure 1-13](image)

**Figure 1-13** Different stages of feature extraction and sample classification in the feature space (Reproduced from [68] with permission from IEEE).
Different feature extraction methods are used and reported in the literature. For instance, the maximum level of the response, difference between maximum and minimum levels, area underneath the response curve, signal peak time, maximum of the differentiation with respect to time, and slope of the response (or linear fitted line) are among these features in the literature [68-73]. The next stage in Figure 1-13 is related to dimension reduction. There are different methods used to reduce the dimensions of the extracted features. These include: linear methods such as Principal Component Analysis (PCA) [74] and Linear Discriminant Analysis (LDA) [75], and non-linear methods such as Kernel Principal Component Analysis (KPCA) [76] and Generalized Discriminant Analysis (GDA) [77]. Among these, PCA is the most popular method. PCA is a statistical method which uses an orthogonal transformation to convert a set of observations (which are possibly correlated variables) into a set of values of linearly uncorrelated variables called principal components. If an efficient method of feature extraction is used, the feature vectors related to different responses can be classified and clustered (in clear-cut clusters) in the feature space. Different methods such as k-nearest neighbor (KNN) [78], neural network (NN) [79], and support vector machine (SVM) [80] are used for data classification, and hence gas identification, in the feature space. KNN is one of the most commonly used methods for sample identification. In this method, the distances of each feature vector to different clusters are measured and based on the measured distances the appropriate cluster (minimum distance) is selected. This method is simple but computationally expensive, and it needs mathematical and analytical tools as the distance of the feature vector from all the other points in the feature map is required to be measured and compared [78].

1.3.3.3 E-nose Applications

There is a wide range of applications for electronic noses. Table 1-1 lists some of the applications explained below:

**Food industry:** The most important area in which e-noses are used is the food sector. E-noses sniff the food which results in valuable judgments about the quality of the food, the types of ingredients used, freshness of the food, the presence of additives, etc. Most research
focuses on detecting dairy products (such as milk [81]), coffee and tea [83-84], edible oils [84], vinegars [85], and meat and fish [86-89].

**Agriculture:** Sniffing agricultural products results in valuable information on their type and quality (whether they are raw and fresh). Most important studies have focused on fruits, plants, vegetables, and composts [95-117].

**Medical:** Another interesting application of e-noses is medical monitoring and diagnostic. Analyzing human exhaled breath, skin odor, and other body odorants have been recently used for both diagnosis of diseases and monitoring the health condition of patients [123-126]. The advantages of breath analysis over other diagnostic techniques (such as blood, skin and urine tests) include fast analysis and minimum discomfort to patients and the users [123]. In this method, the health condition of a patient is determined by evaluating the composition and amount of exhaled VOCs. As biomarkers, a certain level of specific VOCs in the breath often indicates the biological or physiological malfunction due to progression of a disease [123]. For instance, acetone and ethanol are found in the breath of diabetics [127]; pentane level is higher in breath of patients with schizophrenia [128]; high concentrations of methane indicate colon cancer [129], and benzene concentration in the breath is much higher in patients with lung cancer [130].

Another application for e-noses is detection of marijuana or alcohol in breath which has been used as an indicator of cannabis, or alcohol use, respectively [131-132]. However, as there are traces of other VOCs in the breath, it is important to differentiate among different gases, and pinpoint the distinct “smell print” of marijuana or alcohol.

**Safety:** Monitoring the quality of the air and measuring the level of toxic gases are huge demands for e-noses. Among these applications are monitoring the level of carbon monoxide, methane, and other green-house gases (GHG) [158].

**Environmental:** Environmental monitoring is another application of e-noses. These applications include monitoring the quality of water, soil, and air. Detecting contaminants in water, molds in soil, poisonous gases exposed from chemical composts are among a few applications [153-165].

**Robotics:** Developing robots equipped with a sense of smell for pinpointing and detecting the smell is another application of e-noses [171-177]. In space, for instance, e-noses are used for detecting ammonia leakage in the space craft [171-173].
Table 1-1 Different applications of electronic noses.

<table>
<thead>
<tr>
<th>Application</th>
<th>Examples</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food Industry</td>
<td>Coffee, Meat, Fish, Oil, Diary, bread</td>
<td>[81-94]</td>
</tr>
<tr>
<td>Agriculture</td>
<td>Fruit, Cereal, Vegetable, plant, Poultry</td>
<td>[95-117]</td>
</tr>
<tr>
<td>Medical</td>
<td>Disease diagnosis, Breath analysis, Hospital</td>
<td>[118-132]</td>
</tr>
<tr>
<td>Beverage</td>
<td>Fruit juice, Wine</td>
<td>[133-141]</td>
</tr>
<tr>
<td>Air quality</td>
<td>Pollutant, Toxic</td>
<td>[142-152]</td>
</tr>
<tr>
<td>Environment</td>
<td>Contaminations in water and soil</td>
<td>[153-165]</td>
</tr>
<tr>
<td>Military</td>
<td>Explosives, Chemical Warfare Agents, Counter</td>
<td>[166-170]</td>
</tr>
<tr>
<td></td>
<td>terrorism</td>
<td></td>
</tr>
<tr>
<td>Robotic</td>
<td>Remote sensing, Odor source localization</td>
<td>[171-177]</td>
</tr>
<tr>
<td>Space</td>
<td>Shuttle, International Space Station</td>
<td>[178-182]</td>
</tr>
<tr>
<td>Multimedia</td>
<td>Virtual olfactory interfaces</td>
<td>[183-190]</td>
</tr>
<tr>
<td>Fire &amp; Safety</td>
<td>Fire detection, Leakage detection, Combustible</td>
<td>[191-198]</td>
</tr>
<tr>
<td>Biology</td>
<td>Bacteria, Fungal, Microbial Recognition</td>
<td>[199-201]</td>
</tr>
<tr>
<td>Cosmetic</td>
<td>Fragrance, perfume</td>
<td>[202-207]</td>
</tr>
<tr>
<td>Geology</td>
<td>Soil, Volcanic gases</td>
<td>[208-210]</td>
</tr>
<tr>
<td>Petroleum</td>
<td>Fuel Quality, Fuel Leakage, Oil</td>
<td>[211-214]</td>
</tr>
<tr>
<td>Other Industries</td>
<td>Automotive, Paper quality, Cigarette</td>
<td>[215-218]</td>
</tr>
</tbody>
</table>

1.4 Emerging technologies

As it is mentioned before, in gas chromatography, the gas molecules travel along a meter-long channel called the “column”. Along this channel, the different components are separated and detected. Although there has been a prodigious number of efforts to miniaturize GC [219-221], these devices have so far failed to offer a portable and time efficient solution for gas analysis. Another problem associated with these devices is the size and weight of the carrier gas tank, which hinders the device to be fully portable and hand-held. An example of miniaturized GC column which is fabricated on a silicon substrate is shown in Figure 1-14A [222]. This device is used to detect Benzene-Toluene-Xylene (BTX) mixture and the
response is shown in Figure 1-14B. The small dimensions of the device and the long response time can be seen in Figure 1-14.

![Figure 1-14](image)

**Figure 1-14** (A) Miniaturized gas chromatography column fabricated on a silicon substrate. (B) The transient response of the miniaturized GC exposed to a BTX gas mixture (Reproduced from [222] with permission from Elsevier).

Recently, e-noses are used as the detection unit in gas chromatography and mass spectrometry [223-224]. Therefore, hybrid systems, benefiting from the real-time detection capability of an e-nose-based method and the high selectivity of a conventional gas detection technique (e.g., GC or MS) are developed as a powerful tool for gas detection [60]. Optoelectronic nose is another example of new approaches used for identification of different gases [224-226]. For instance, a simple colorimetric sensor array that detects a wide range of VOCs has been developed. The sensor consists of a disposable array of cross-responsive nanoporous pigments with colors that are changed by diverse chemical interactions with analytes. The pattern of the color change for the array is a unique fingerprint for each VOC. Clear differentiation among 19 different toxic industrial chemicals (TICs) was demonstrated using this technology [225]. The pattern of the colorimetric array of 36 pigments towards 10 different VOCs are shown in Figure 1-15. As it can be seen the color code for each gas is different.
Among the newest e-nose technologies are cyber noses in which an array of biological sensors such as animal olfaction sensory parts (for example worms and mosquitoes) are used [227]. The high sensitivity of animal olfaction system is replicated in a cyber nose in order to be able to detect the faintest molecular traces of chemical vapors.

Despite the real-time detection capability of such systems, the drift of array components in e-nose systems leads to faulty measurement and malfunction of the device [228-230]. The high number of sensors used in e-noses also increases the overall cost of the systems and adds complexity to the calibration of the system. Additionally, since the general-purpose gas sensors are not selective among different gases, the sensor array used in e-noses is required to have different specific sensors for detecting different target gases. This makes the drift compensation and sensor recalibration even more complicated [230].

Single sensor gas detectors (which can also be used as a quasi-array [231]) offer a high level of sensitivity to a wide range of different gases. Calibration of single sensor-based devices is much easier than other conventional methods. Moreover, the fabrication and maintenance cost of such technology is less than GC/MS and electronic noses as their parts do not require frequent replacement and recalibration. The drift compensation for these devices is much simpler than e-noses due to the fact that there is only one sensor in the configuration of these devices as oppose to an array of sensors. One of the most common types of gas sensors used...
in such technologies is MOS gas sensors [232-236]. The off-the-shelf versions of these sensors are inexpensive, durable and have high sensitivity; however, they lack selectivity among different gases, and they also fail to detect different components of a complex odor (or gas mixtures). Recently, it has been shown that a general-purpose gas sensor integrated with a microchannel can be used as a powerful tool for single gas detection [237-241] and also mixtures of different gases in binary or triple mixtures [242]. In essence, based on different molecular diffusion and also adsorption and desorption rates (referred to as “physisorption”) of the gas molecules to the channel walls, the device is able to differentiate among different gases. These devices are also called “microfluidic-based gas detectors” [60]. Microfluidics is a relatively new branch of science that deals with the synthesis and analysis of fluids in a micrometer scale. It offers a noticeable route for miniaturization of chemical and biological processes in “lab-on-a-chip” and “micro total analysis systems” configurations. Microfluidic systems require smaller samples, less time, and smaller equipment for analysis with remarkably high resolution and sensitivity [243]. The microfluidic-based gas detector developed in this project is discussed in details in the next chapters. In Figure 1-16A and B, the schematic of the channel-attached gas sensor and the transient responses of the sensor to four target gases including: hydrogen, butanol, methanol and ethanol are shown.

![Schematic of the channel-attached gas sensor](image1.png)

**Figure 1-16** (A) Schematic of the channel-attached gas sensor. (B) Transient responses of the sensor to four different analytes (Reproduced from [249] with permission from IEEE).
1.5 Challenges and motivation

Although channel-based gas detectors are selective to different gases, they cannot differentiate among components of complex mixtures at low concentrations. Moreover, due to the slow process of gas diffusion in the microchannel and also chemical adsorption of gas molecules to the channel walls, the recovery process of fabricated sensors takes relatively long time (at least 15 min) [237]. Therefore, such technology needs to be further analyzed to optimize the absorption process and enhance the sensitivity and recovery time (referred to as efficiency). Moreover, the effects of polarity of the channel coating and its correlation with the nature of the target gas are still unknown and required to be studied. Such study is crucial; for example, to identify different components of binary or complex gas mixtures, the polarity of the components and coating material plays a crucial role in the sensor discrimination between different components. Another challenge associated with the channel-based gas detection technique is that any fluctuations in the operating conditions of the sensor (including temperature and humidity) dramatically affects the sensor response and the selectivity of the device. Therefore, development of an appropriate humidity and temperature control system is crucial. Finally, it is important to assess the range of the capability of such technology in different applications such as food and beverage identification, medical monitoring devices, and safety and environmental monitoring (which are among the major applications of gas analysis).

1.6 Objectives

This research aims at the development and integration of low-cost, portable, and highly selective and efficient (with fast recovery time and high sensitivity) gas sensor into continuous and digital microfluidics platforms for detection of gas and liquid VOCs, respectively. The diagnostic power of the developed sensors is enhanced in order to be able to differentiate small concentrations (ppm level) of different VOCs. A range of different target analytes from alcohol and ketone, to alkane vapors are tested and successfully differentiated. The main advantage of the proposed device over previous microfluidic-based gas sensors [234-237] is the enhanced selectivity by implementing novel surface coating and optimizing the microchannel geometry. Moreover, studying the interaction between the analyze and channel wall surface coating resulted in reducing the sensor recovery time to 150
seconds [60], as opposed to over 15 minutes reported in previous studies [237]. A humidity control system is also introduced which is compatible with the proposed diffusion-based gas analysis technique. A range of different gases are tested and the performance of the gas detector is compared in presence and absence of the humidity control system.

1.7 Organization of thesis

The above objectives will be achieved through the following specific chapters in this thesis: 2) theory (diffusion-physisorption), 3) experimental setup, 4) multilayer coating and dimension characterization for the diffusion-based microfluidic-integrated gas sensors to detect small concentrations of VOC analytes, 5) selective detection of volatile organic compounds in microfluidic gas detectors based on “like dissolves like”, 6) design and implementation of a humidity control system to decrease the effect of humidity on the sensor, and 7) assessing the range of the capability of the gas detector in applications including: (a) digital microfluidic-based gas detectors to manipulate, analyze and differentiate different wine samples in liquid phase; (b) microfluidic-based THC analyzer for potential monitoring of cannabis use in the exhaled breath; and (c) diffusion and flow-based microfluidic gas detectors for natural gas leakage detection along pipelines.
Chapter 2  Theory (Diffusion-physisorption Equation)\textsuperscript{1}

Current gas sensors are either made to be evenly sensitive to different gases or fabricated for detecting a specific target. Hence, differentiating among different gases or a mixture of gases using a single sensor is very challenging, as the transient responses of the sensor to two different gases are almost the same. The schematic of a MOS gas sensor and its bias circuit and responses of the sensor to two different gases are depicted in Figures 2-1A and 2-1B. To enhance the selectivity of the gas sensor, it can be integrated into a microfluidic channel. The schematic of a MOS gas sensor equipped with a channel and its bias circuit is shown in Figure 2-1C. The kinetic responses of the microfluidic-based gas sensor for two different gases are distinct (see Figure 2-1D). The response profile of a microchannel-based gas sensor is dependent on the analyte diffusivity in the surrounding media of the channel (air), and the physical adsorption/desorption of the gas molecules to/from the channel walls (see Figure 2-1E).

The analyte concentration profile along the channel, $C(x, t)$, is changed by diffusion of the gas molecules into the channel. In channels with dimensions of a few millimeters and more (not microfluidic channels), diffusion of the gas molecules along the channel is the most dominant parameter which defines the change in the analyte concentration along the channel. This can be mathematically described through the diffusion equation \textsuperscript{[246]}:

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2}$$  \hspace{1cm} (3)

in which $D$ is the analyte diffusion coefficient (diffusivity) in air \textsuperscript{[247]}. By decreasing the channel depth to less than one millimeter, the ratio of the surface to volume along the diffusion channel increases, and hence, a large number of gas molecules adsorb to the surface of the channel. This can be mathematically predicted by the solutions of the following equation \textsuperscript{[248-249]}:

\textsuperscript{1} Parts of this chapter have been published as a full paper in Sensors and Actuators B:Chemical.
Figure 2-1 (A) The schematic of a MOS gas sensor and its bias circuit exposed to two different gases. (B) The typical transient responses of the sensor for two different gases (red and blue) are almost the same. (C) The schematic of a MOS gas sensor equipped with a channel and its bias circuit exposed to two different gases. (D) The typical transient responses of the microfluidic-based gas sensor for two different gases (red and blue) are distinct. (E) The sensor integrated with a microchannel on a 3D printed platform. Analyte molecules diffusion into the channel, some of the molecules get adsorbed and some of the adsorbed molecules get desorbed (Reproduced from [60] with permission from Elsevier).
\[ \frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} - \frac{\partial C_s(x,t)}{\partial t} \]  

(4)

in which \( C_s \) is the concentration of the gas molecules, adsorbed to the surface of the channel. This number is related to the type of the gas molecule and the features of the channel inner surfaces. The channel is assumed to be positioned along the \( x \)-axis and the channel inlet is placed at \( x=0 \) and the sensor is placed at \( x=l \), where \( l \) presents the length of the channel. The concentration loss due to adsorption (\( C_s(x,t) \)) can be obtained as

\[ C_s(x,t) \, dV = \theta(x,t) \, C_a \, dA \]  

(5)

In this equation, \( C_a \) is the surface density of the adsorption sites and \( \theta \) is the fractional surface coverage defined as the ratio of the occupied adsorption sites to the number of all adsorption sites (see the following relation).

\[ \theta(x,t) = \frac{\alpha C(x,t)}{1 + \alpha C(x,t)} \]  

(6)

In the above equation, \( \alpha \) is the modified Langmuir coefficient [250]. The differential volume and surface are defined as

\[ dV = Wd \, dx \]  

(7)

\[ dA = 2(d + W) \, dx \]  

(8)

where \( W \) and \( d \) present the width and depth of the channel, respectively. Substituting Equations (7) and (8) into (5) results in

\[ C_s(x,t) = C_a \frac{2(W+d) \, dx}{Wd \, dx} \, \theta(x,t) \quad \Rightarrow \quad if \ W \gg d : C_s(x,t) = \frac{2C_a}{d} \theta(x,t) \]  

(9)

Substituting Equation (6) into (9) yields

\[ C_s(x,t) = \frac{2C_a}{d} \frac{\alpha C(x,t)}{1 + \alpha C(x,t)} \]  

(10)
Combining the diffusion equation and adsorption equation results in “diffusion–physisorption” equation, this gives the analyte concentration change (over time) along the channel.

\[
\left(1 + \frac{2C_a}{d \left(1 + \alpha C(x,t)\right)}\right) \frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2}
\]

(11)

The theory of diffusion/physisorption of gas molecules along/to the channel walls were presented and the concentrations of gas molecules along the micro channel were mathematically predicted by deriving diffusion-physisorption equation. Eq. (11) is derived based on Langmuir model [250], which is not totally accurate as it has some limitations such as: it assumes mono layer adsorption of gas molecules to the surface. In order to make this model more reliable someone could consider multi-layer adsorption of gas molecules to the channel surface which can result in more complex equations.
Chapter 3 Experimental setup and device fabrication

3.1 Gas detector setup

The schematic diagram of the experimental setup is shown in Figure 3-1A. This shows the general configuration of the experimental setup. In the future chapters, depending on the purpose of each study, the setup has been changed and presented in each chapter. The device consists of a gas chamber, 3D printed microfluidic channel, and gas sensor. The sample (in this case in a liquid phase) is injected into the chamber through its opening using a precise Pipet-Lite XLSmicro sampler (the analyte injection stage shown in Figure 3-1B1). After a few minutes, the sample is evaporated and fills the chamber. The sensor is rotated around the hinge and exposed to the chamber (filled with the target gas) for 40 seconds (the exposure stage shown in Figure 3-1B2). This time is chosen based on the sensor type and the range of gas concentration used here, in a way not to saturate the sensor. The gas molecules diffuse into the channel and reach the sensing pallet of the sensor, which is placed at the other end of the channel. There is competition between diffusion and adsorption of the gas molecules to the available adsorption sites on the channel walls, which together make the device selective among different gases as each gas has its specific “smell-print” on the sensor. Finally, the sensor is rotated back to its original position where it is exposed to the clean air again and the gas molecules diffuse out from the channel (the recovery stage shown in Figure 3-1B3). The data is collected (using a microprocessor) until $t=100$ s. The device remains 150 seconds in this position till the sensor fully recovers and becomes ready for the next experiment.

The initial and boundary conditions imposed by the device structure and the measurement method utilized are [237]:

$$C(0, t) = C_0 \quad 0 < t < t_e \quad (12)$$

$$C(x, t) = 0 \quad 0 < x < L, \quad 0 < t < t_e \quad (13)$$

$$\frac{\partial C}{\partial x} = 0 \quad x = L \quad (14)$$

---

2 Parts of this chapter have been published as a full paper in Sensors and Actuators B: Chemical.
Solutions of Equation (11) from chapter 2 predict the analyte concentration along the channel for the time period of \( t_e = 40 \) s after which the channel is reconnected to the clean air for recovery. During this process, analyte molecules desorbed from the channel and micro-cavity walls diffuse out from the channel inlet. The analyte concentration profile along the channel during this period is also predicted by Equation (11), but with the initial conditions listed below:

\[
C(0, t) = 0 \quad t > t_e 
\]

\[
C(x, t_e^-) = C(x, t_e^+) \quad 0 < x < L
\]

\[
\frac{\partial C}{\partial x} = 0 \quad x = L
\]

In the above equations, \( C(x, t_e^-) \) is calculated from the diffuse-in solutions of Equation (11) for \( t = t_e \). Hence, \( C(x, t) \) during the time analysis of 100 s is predicted from the solutions of Equation (11) using two (above-mentioned) different sets of initial conditions.

### 3.2 Feature extraction

The obtained (typical) normalized transient response of the sensor to a typical gas concentration is shown in Figure 3-1B. The normalization process eliminates the effects of the analyte concentration and baseline variations from the responses. Using Equation (18), the change in the sensor conductance \((G(t))\) is normalized between 0 to 1 [60].

\[
G_n(t) = \frac{G(t) - \min(G(t))}{\max(G(t)) - \min(G(t))}
\]  

The method described in [243] is used here for feature extraction: three significant points (features shown in Figure 3-1B) including those that present the times at which the normalized response level reaches 0.05 and 0.95 (referred to as \( t_r \) and \( t_m \), respectively) and the magnitude of the normalized response at the final read out \((R_f)\) are extracted from each response. A 3-D feature space is defined based on \( t_r \), \( t_m \), and \( R_f \), where each response is depicted as a point \((t_r, t_m, R_f)\). The atmosphere air of the laboratory (with temperature 25±1°C and relative humidity of 40±5%) is the background media for most experiments otherwise mentioned.
3.3 Fabrication process

The fabrication process for each component of the system is explained here:

3.3.1 Gas sensor

A commercially available tin oxide-based chemoresistive gas sensor (SP3-AQ2, FIS Inc., Japan) is used in this study [243]. The nominal operating temperature is 300˚C maintained by applying 5V DC to the microheater (the bias circuit for the sensor is shown in Figure 1-12B).

3.3.2 Microchannel

The microchannels and micro-chambers are printed with a 3D printer (Connex 500) using the material VeroClear RGD810 (see Figure 3-2). To study the effect of the channel dimension on the selectivity and time efficiency of the sensors, different devices are printed with different channel sizes (see Chapter 4).

3.3.3 Channel Coating

The inner surfaces of the microchannels are coated with single layers and multi-layer combinations of different materials including: gold (with a layer of chromium for adhesion), copper, Cytonix (Cytonix LLC, Product: PFCM 1104V), and Parylene C (poly (p-xylylene) polymer, CAS No: 28804-46-8). The total number of 11 sensors (see Chapter 4) are made using different material combinations as for the channel coating. For some of the targets such as Au, Cr, Cu, and SiO₂, the channel surfaces are coated using physical vapor deposition (PVD) sputtering machine (Angstrom Engineering, Nexdep deposition system). Parylene C is coated using a chemical vapor deposition (CVD) Parylene C coating machine (SCS. PDS 2010 Labcoater). For Cytonix, the dip coating and spin coating methods are both used. Figure 3-2 shows a typical channel coated with multi-layer materials including 65 nm gold (with a 35-nm layer of chromium underneath) and 4 μm Parylene C.

3.3.4 Chamber

A small opening on the chamber (made of Polymethyl methacrylate (PMMA)) is provided for both analyte injection and purging clean air into the chamber. An electric fan (DC Brushess. DC24V. 1.41A. Delta Electronics) is installed in the chamber to make a uniform environment inside the gas chamber. The microchannel is attached to the chamber using a screw hinge, which allows the device to rotate on the chamber.
Figure 3-1 (A) The schematic of the experimental setup. The sensor is mounted on a 1 liter PMMA chamber. (B) Three different phases of an experiment and a typical normalized transient response of the sensor to a concentration of a gas (B1: analyte injection stage, B2: exposure stage, and B3: recovery stage) (Reproduced from [60] with permission from Elsevier).
Figure 3-2 The schematic diagram of the 3D printed gas sensor. The channel is coated with chromium, gold, and Parylene C. The above mentioned coating combination shows the best selectivity among others (see Section 4.2) (Reproduced from [60] with permission from Elsevier).
Chapter 4 Development of a diffusion-based microfluidic gas detector: multilayer coating and dimensional characterization

Here a low-cost, portable, and highly selective 3D-printed gas sensor for detection of different VOCs is presented [60]. A 3D printed continuous microfluidic platform is fabricated by integrating a chemoresistor with a microfluidic channel. Here, the effects of different coating materials inside the channel and the channel dimensions on the diffusion-physisorption of gas molecules along the channel are studied. The diagnostic power of the developed miniaturized gas sensors and the time recovery of the sensors are compared. An optimized channel with a unique coating and geometry is then proposed.

To study the effect of channel dimensions and channel surface treatment on the selectivity and time recovery of the sensors, different devices are printed with different channel sizes and coated with different materials. Channels with six different dimensions including three lengths (2 cm, 3 cm, and 4 cm) and two heights (200 µm and 500 µm) are fabricated. The width of the channel of 3 mm (limited to the dimensions of the sensor chamber) is kept for all devices. The total number of 11 sensors (listed in Table 4-1) are made using different material combinations as for the channel coating.

4.1 Channel coating

The analyte diffusion process is independent of the channel’s coating material. However, the adsorption and desorption processes are dependent on both gas type and the channel surface material. Therefore, it is expected that the surface treatment of the channel results in different transient response profiles. To study the effect of channel coating on the sensor response, a set of materials (listed in Table 4-1) are tested.

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3 Parts of this chapter have been published as a full paper in Sensors and Actuators B: Chemical.
Table 4-1: Different channel coating materials used for fabricating the sensors.

<table>
<thead>
<tr>
<th>Number</th>
<th>Single layer/multilayer coating</th>
<th>Coating Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VeroClear RGD810</td>
<td>No coating (3D printed material)</td>
</tr>
<tr>
<td>2</td>
<td>Copper (Cu)</td>
<td>Sputtering</td>
</tr>
<tr>
<td>3</td>
<td>Chromium (Cr) &amp; Gold (Au)</td>
<td>Sputtering</td>
</tr>
<tr>
<td>4</td>
<td>Parylene C</td>
<td>CVD</td>
</tr>
<tr>
<td>5</td>
<td>SiO$_2$</td>
<td>Sputtering</td>
</tr>
<tr>
<td>6</td>
<td>Cytonix</td>
<td>Spin Coating</td>
</tr>
<tr>
<td>7</td>
<td>Cu &amp; Cytonix</td>
<td>Sputtering (Cu) &amp; Spin coating (Cytonix)</td>
</tr>
<tr>
<td>8</td>
<td>Cr &amp; Au &amp; Cytonix</td>
<td>Sputtering (Cr and Au) &amp; Spin coating (Cytonix)</td>
</tr>
<tr>
<td>9</td>
<td>Cu &amp; Parylene C</td>
<td>Sputtering (Cu) &amp; CVD (Parylene C)</td>
</tr>
<tr>
<td>10</td>
<td>Cr &amp; Au &amp; Parylene C</td>
<td>Sputtering (Cr and Au) &amp; CVD (Parylene C)</td>
</tr>
<tr>
<td>11</td>
<td>SiO$_2$ &amp; Parylene C</td>
<td>Sputtering (SiO$_2$) &amp; CVD (Parylene C)</td>
</tr>
</tbody>
</table>

Normalized transient responses of six of the sensors (coatings number 3-4 and 8-11) to 2000 ppm ethanol are shown in Figure 4-1. The rest of the channel coatings (coatings number 1-2 and 5-7) do not show significant responses as some of the materials hinder the diffuse-in process. In other words, these five coatings trap all the ethanol molecules, preventing the transport of the gas molecules along the channel and towards the sensor. As it can be seen in Figure 4-1, the interaction of the gas molecules with different materials is different resulting in varying normalized responses.

4.1.1 Metal layer

Among all the channels coated with single metal layers, gold has the best response, as it is one of the most non-reactive materials in nature and used here to decrease the chemical cross contamination of the gas molecules to the channel walls which eventually results in faster sensor recovery. The chromium layer is coated to increase the adhesion of the substrate to gold.
Figure 4-1 Normalized responses of six sensors with six different coating material combinations deposited on the channel to 2000 ppm ethanol (Reproduced from [60] with permission from Elsevier).

### 4.1.2 Bottom layer
In the case of channels with multilayer coatings, it is observed that the channels coated with different bottom layer materials (even with the same top layer) provide different responses. For instance, the channel coated with three layers of Cr, Au, and Parylene C (with a gold and chromium layer as the bottom coating layers) and Cu and Parylene C (with the copper layer as the bottom coating layer) show different responses to the same concentration of an analyte (e.g., ethanol). This is due to the permeation of the gas molecules through the top layer and reaction with the bottom coating layer.

### 4.1.3 Top layer
The preliminary experiments revealed the importance of the porosity of the top coating layer. In essence, the number of surface adsorption sites available per unit volume of the channel ($C_a$ in Equation (11)) is greater in channels with higher porosity. As it is shown in Figure 4-1, the diffuse-in and out processes of ethanol are significantly rapid in the channels with the combination of Cr and Au and Parylene C coatings; whereas, the coating combination of Cr and Au and Cytonix shows the slowest response which means more adsorption occurs in the case of Cr and Au and Cytonix channel coating. Thus, Parylene C is a great candidate for the
top layer coating material as it can be coated as a thin polymer film, which is chemically inert. Also, it has high porosity with small pore sizes [251], which increases physical adsorption of the gas molecules to the channel walls that eventually increases selectivity of the sensor. In addition, Parylene C provides a pinhole free coating and lower permeability (as compared to other similar polymers) and has been recently used in the development of GC columns [252] as well as a material for moisture barrier in numerous applications [253]. The latter is critical for gas sensing since the gas sensors are subject to errors as they are vulnerable to ambient fluctuations such as humidity and temperature change. Therefore, the response of a sensor depends on not only the analyte concentration, but also the ambient conditions (particularly humidity). In high precision sensing applications, such as breath analyzers, fluctuation in humidity can result in false signals. Thus, the use of a strong moisture barrier such as Parylene C along the channel can reduce the error caused by humidity.

4.1.4 Analytes

Three different analytes including ethanol, methanol, and acetone are tested to compare the selectivity of the fabricated sensors among different gases. These gases are selected to show the capability of the device in differentiating alcohol and ketone vapors. Four out of the eleven fabricated sensors showed acceptable selectivity among the three selected analytes. The temporal responses obtained from the device are normalized to fit within the magnitude range of [0 1], eliminating the influence of the analyte concentration on the shape of the responses. Normalized responses for each of the sensors to 2000 ppm of each of the three analytes are shown in Figure 4-2. Each of the four sensors give unique responses corresponding to different tested analytes. In other words, the fingerprint of three analytes on each of the four selected sensors are distinct, however, different sensors distinguish these three analytes differently. In other words, from one sensor to another, the level of segregation between analytes is different, showing different selectivity among the sensors tested. A better quantitative comparison can be performed based on calculating indicators of selectivity and the recovery time of the sensors. This comparison will lead to identifying the optimum material for the treatment of the channel. For instance, Figure 4-3 shows typical responses of one of the sensors (which later will be shown that it is the optimum one in terms of the indictors) against three different analytes. A selectivity factor is defined as $S=S_1+S_2+S_3$, in
which $S_1$, $S_2$, and $S_3$ are the absolute values of the distances between the amplitude of responses of methanol-acetone, ethanol-methanol, and acetone-ethanol, respectively, at five different time points ($t=20s$, $t=40s$, $t=60s$, $t=80s$, and $t=100s$). The square root of the sum of square of the selectivity factors at five points is used as a measure of selectivity of different sensors. Another factor for determining the sensor performance is the recovery time: in essence, the sensor with the lower recovery time is preferable.

4.1.5 Optimum coating

The selectivity and recovery time of the fabricated sensors are all compared and listed in Table 4-2. In this table, the sensors are listed based on two major categories: coating materials and dimensions. The average pick time of each sensor, which is the mean of three time points for which the sensors have the maximum readout for three different analytes, are also calculated and listed. It is observed that the smaller the pick time value the faster the recovery of the sensor. The average pick time is used to rank (in the order of 1 to 4, from the lowest average pick time to the highest, respectively), and hence to compare the speed of the recovery of different detectors. The sensors are also ranked based on their selectivity factor (as explained above). The effect of both coating materials and channel dimensions were separately investigated through the above ranking schemes. The results show that the Cr and Au and Parylene C coated sensor provides the maximum selectivity and the minimum recovery time among all the coating materials tested here. This means that the proposed coating combination decreases the cross contamination and the chemical adsorption and increases the physical adsorption (and hence selectivity). To perform a quantitative comparison of the response of the sensor to different analytes, three features ($t_r$, $t_m$, $R_f$) are extracted from each normalized response. The feature space for the sensor with the coating combination of Cr and Au and Parylene C, which shows the best performance in terms of selectively and recovery time, is shown in Figure 4-4.
Figure 4-2 Normalized responses for three different analytes for four different channel coatings. (A) SiO$_2$ and Parylene C, (B) Cr and Au, (C) Cu and Parylene C, (D) Cr and Au and Parylene C (Reproduced from [60] with permission from Elsevier).
**Figure 4-3** Typical normalized responses for three different analytes; the selectivity factor is defined to show the differentiation power of the sensor (Reproduced from [60] with permission from Elsevier).

**Table 4-2** Comparison of the separation factor and recovery time of the fabricated sensors.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Channel Length (l)</th>
<th>Channel Depth (d)</th>
<th>Average peak time (sec.)</th>
<th>Rank</th>
<th>Selectivity factor (S)</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sensors with Different Coatings</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-Au-ParyleneC</td>
<td>30mm</td>
<td>500µm</td>
<td>59.37</td>
<td>1</td>
<td>1.49</td>
<td>1</td>
</tr>
<tr>
<td>Cr-Au</td>
<td></td>
<td></td>
<td>154.07</td>
<td>4</td>
<td>1.07</td>
<td>3</td>
</tr>
<tr>
<td>SiO₂-ParyleneC</td>
<td></td>
<td></td>
<td>72.25</td>
<td>2</td>
<td>1.08</td>
<td>2</td>
</tr>
<tr>
<td>Cu-Parylene C</td>
<td></td>
<td></td>
<td>98.51</td>
<td>3</td>
<td>1.01</td>
<td>4</td>
</tr>
<tr>
<td><strong>Sensors with Different Dimensions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-Au-Parylene C</td>
<td>20mm</td>
<td>500µm</td>
<td>51.18</td>
<td>1</td>
<td>1.37</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>30mm</td>
<td>500µm</td>
<td>59.37</td>
<td>2</td>
<td>1.49</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>40mm</td>
<td>500µm</td>
<td>67.25</td>
<td>3</td>
<td>1.52</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>30mm</td>
<td>200µm</td>
<td>68.56</td>
<td>4</td>
<td>1.74</td>
<td>1</td>
</tr>
</tbody>
</table>
The feature space for the sensor with the coating combination of Cr and Au and Parylene C, which shows the best performance in terms of selectively and recovery time (Reproduced from [60] with permission from Elsevier).

4.2 Channel dimensions

After choosing the best coating combination among all the materials listed in Table 1, which is Cr and Au and Parylene C, sensors with three different channel lengths and two different channel depths are fabricated and tested (see Table 4-2). The ranking procedure explained above was also used to quantify the effect of the channel dimension on selectivity and the recovery time. In general, there is an opposite trend in rankings based on the selectivity and recovery time for sensors with different dimensions. This fact is explained in detail below.

4.2.1 Channel depth

Normalized responses for three different analytes (ethanol, methanol, and acetone) tested with four different channel dimensions (i) $l=20$ mm, $d=500$ μm, (ii) $l=30$ mm, $d=500$ μm, (iii) $l=40$ mm, $d=500$ μm, and (iv) $l=30$ mm, $d=200$ μm ($l$ is the length and $d$ is the depth of the channel)) are depicted in Figure 4-5. As expected, the sensors with larger channel depths are recovered faster. According to Equation (11), increasing the depth of the channel decreases the effect of physical adsorption which will result in changing the diffusion-physisorption equation to a diffusion equation (Equation 3) for deep channels. In this case (which is only diffusion dependent), the only analyte related parameter in the equation is $D$ (gas diffusivity). On the other hand, by decreasing the channel depth, the effect of $C_\alpha$ and $\alpha$ in Equation (11)
increases and more adsorption and desorption dependency will be observed in the response. Thus, channels with smaller depths are recommended to differentiate gases with similar diffusion coefficients.

4.2.2 Channel length

In case of examining two gases (with different diffusion coefficients), increasing the length of the channel increases the diffusion time, which results in a larger difference in the temporal responses of the sensor (see Figure 4-5). In other words, increasing the length of the channel slows down the diffusion process and increases the selectivity of the sensor. However, longer channels result in a longer recovery time for the sensor. Therefore, considering the trade-off between selectivity and the recovery time of the sensor the optimum dimension of the channel is $l=\text{30 mm}$, $d=\text{200 }\mu\text{m}$ (see Table 4-2).

4.2.3 Analyte concentration

After optimizing the sensor coating and dimensions, the channel with the coating combination of Cr and Au and Parylene C and the dimensions of $l=\text{30 mm}$ and $d=\text{200 }\mu\text{m}$ was used for verifying the selectivity of the sensor. A wide range of concentration (250-4000 ppm) of 6 different target gases are selected among alcohols (including 2-pentanol, ethanol and methanol) and ketone vapors (including acetone, 2-butanone and 2-pentanone). The transient responses for 8 different concentrations of 6 different targets is shown in Figure 4-6. The sensor differentiates among different concentration of gases. As presented in Figure 4-7, the feature space shows the analytes are successfully separated in the 3D space. The feature vectors of the responses related to each analyte at different concentrations form a clear-cut cluster in the feature space (see Figure 4-7). The three selected features are: the time at which the normalized response level reaches 0.05, the time at which the normalized response level reaches 0.95, and the magnitude of the normalized response at the final read out. No mathematical tool is needed for mapping the responses into the feature space, and only one simple feature extraction method is adequate for the determination of the positions of the target analytes in the feature space. The feature space of a particular device is universal and undergoes hardly any modifications when applied to different analytes.

The gas detector operation depends on ambient humidity and temperature. Ambient temperature and humidity dependence of the responses provided for a specific analyte may be considered as sources of error, which causes displacement of the feature vector related to
each analyte in the feature space. This arises from the fact that the analyte diffusion/physisorption along the channel/to the channel walls are both strongly temperature-dependent processes. These errors caused by ambient fluctuations introduce drift-like terms into the responses of the sensor, which causes false measurements. Therefore, the ambient temperature and humidity must be controlled during all the experiments (see Chapter 6).

![Normalized responses for three different analytes (acetone: blue, ethanol: red, and methanol: green) for four different channel dimensions. (A) \( l=20 \text{ mm}, d=500 \mu\text{m} \), (B) \( l=30 \text{ mm}, d=500 \mu\text{m} \), (C) \( l=40 \text{ mm}, d=500 \mu\text{m} \), and (D) \( l=30 \text{ mm}, d=200 \mu\text{m} \) (Reproduced from [60] with permission from Elsevier).](image)

**Figure 4-5** Normalized responses for three different analytes (acetone: blue, ethanol: red, and methanol: green) for four different channel dimensions. (A) \( l=20 \text{ mm}, d=500 \mu\text{m} \), (B) \( l=30 \text{ mm}, d=500 \mu\text{m} \), (C) \( l=40 \text{ mm}, d=500 \mu\text{m} \), and (D) \( l=30 \text{ mm}, d=200 \mu\text{m} \) (Reproduced from [60] with permission from Elsevier).
Figure 4-6 Recorded transient responses for 8 different concentrations (250 ppm-4000 ppm) of 6 different targets including three alcohols ((A) 2-pentanol, (B) methanol, (C) ethanol) and three ketones ((D) acetone, (E) 2-butanone, and (F) 2-pentanone) (Reproduced from [60] with permission from Elsevier).
Figure 4-7 Feature space presentation for all the responses shown in Figure 4-6 (Reproduced from [60] with permission from Elsevier).

A different method of feature extraction is also used for characterization of the concentration of the analyte. Three different features are extracted from each transient response (see Figure 4-8A). The signal maximum response level ($F_1$), the response level for the final readout ($F_2$), and the surface area underneath the response ($F_3$) are the three extracted features from each transient response. The feature vector ($\Phi$) extracted from the transient response is shown in a 3D space in Figure 4-8B. The transient responses of the sensor with Cr and Au and Parylene C channel coating and dimensions of $l$=40 mm, $w$=3 mm, $d$=500 $\mu$m are shown in Figure 4-9A. The transient responses represent the repeatability of the device for each concentration. Some parts of the transient responses are magnified to show the reproducibility of the response for each concentration. The feature vectors related to each concentration are segregated (see Figure 4-9B) in the feature space. The results show three separated spheres, representing the separation capability of the device between different concentrations of the same analyte. A regression model is used to show the linear relation between the concentration and the area underneath the curve (see Figure 4-10).
Figure 4-8 (A) a typical transient response of the sensor to a concentration of a gas. (B) The feature extraction method used for identification of the concentration of the analyte is presented. Three selected features are the maximum level of the transient response ($F_1$), the response level at the final readout ($F_2$), and the area under the transient response curve ($F_3$) (Reproduced from [60] with permission from Elsevier).
Figure 4-9 (A) The transient response of the sensor to three different concentrations of ethanol, i.e., 1000 ppm (blue), 2000 ppm (red), and 3000 ppm (green). (B) The feature space (using the method described in Figure 4-8) is presented for identification of the concentration of the analyte (Reproduced from [60] with permission from Elsevier).
The regression model used for characterization of the concentration of the analyte ($C$) with respect to the area underneath the transient response curve ($A$). The relation between the concentration and the average of the area underneath the curves is linear. Each square marker is the average of 5 points and the error bars present the standard deviation from the average (Reproduced from [60] with permission from Elsevier).

**Figure 4-10**

**4.3 Summary**

A 3D-printed microfluidic platform was fabricated by integrating a chemoresistor within a channel. Using a novel coating combination, a surface treatment on the inner walls of the microfluidic channel was carried out, which enhances the selectivity power of the device. Different coating materials were tested and compared to choose the best material in terms of giving the maximum selectivity and the minimum sensor recovery time. The geometry of the channel was optimized after comparison of the results of sensors fabricated with different channel dimensions. Using a new feature extraction method, a regression model was proposed to relate the concentration of the analyte to the features obtained from the transient response of the sensor (resulted from varying the concentration of the analyte).
Chapter 5  Selective detection of volatile organic compounds in microfluidic gas detectors based on “like dissolves like”  

So far it has been shown monitoring the molecular diffusion of gas along a few centimeters-long and few micrometer-deep channels (or capillaries) results in gas identification due to diffusion-physisorption of gas molecules which is also intensified with the special geometry of the channel (high surface area to volume ratio) [243]. Moreover, it has been shown that optimizing the micro-channel geometry and surface treatment can significantly enhance the selectivity of microfluidics gas detectors which results in higher order gas analysis [60]. Combination of chromium, gold, and Parylene C is introduced for its particularly high selectivity and low sensor (channel) recovery time [60]. Despite these enhancements, the interaction between the target gases and surface of the microchannel has not yet been fully understood and determined in a quantitative manner. More specifically, the effect of the channel coating (and specifically its correlation with polarity of the target gas) on differentiation of different components of binary or complex gas mixtures is still unknown. Understanding these interactions is crucial for determination of an optimum coating [254] (directly affecting selectivity of the sensor) for different target gases.

In this chapter, the effects of channel hydrophobicity on the selectivity of the microfluidic-based gas detector for different VOCs are studied. Two different channel coating combinations with two different levels of hydrophobicity are compared. These coating combinations are referred to as (i) Detector O which includes chromium, gold, Parylene C, and (ii) Detector X containing chromium, gold, Parylene C, Cytonix. A variety of target gases from different families of VOCs (including alcohols (methanol, ethanol, 1-propnaol, 2-pentanol), ketones (acetone), and alkanes (pentane, hexane)) are chosen for this study. The goal is to show how the classical “similia similibus solvuntur” or “like dissolves like” principle is applied here. In essence, the differentiation of compounds along the microchannel of a microfluidic-based gas detector [60] is based on the different strengths of the interaction of the compounds with the surface of the channel walls (“like dissolves like” rule). The stronger this interaction the longer the time for the analyte to migrate through the

4 Parts of this chapter have been submitted as a full paper to Analytica Chimica Acta.
channel (by the mode of diffusion) and reach the sensor. To study the effect of this interaction, three methods are used: first, the responses of two detectors (O and X) and their selectivity is compared (using the normalized and feature space responses of these two detectors to a range of different target gases). Then, a second study is conducted on the effects of channel coating and analyte polarity on the detectors responses. Finally, the channel surface free energy of these two fabricated detectors is determined to quantify the analyte/channel interaction and verify the outcomes of the previous two methods. The result of this chapter can be used for proper selection of channel coating based on the polarity of the target analytes.

5.1 Experimental Method

5.1.1 Gas detector setup

The experimental setup consists of three major parts (see Figure 5-1): a one-litter Poly-methyl methacrylate (PMMA)-based gas chamber for sample injection (sampling chamber), two 3D-printed gas detectors with different coating materials (see below), and two 3-way manual valves connecting the detectors to the chamber or to clean air (laboratory environment). The detectors are made of VeroClear RGD810 material and connected to three way valves and placed on the top plate of the chamber. The PMMA chamber (which is fully sealed to prevent leakage of the gas molecules) is used as a gas sample injection container and for exposing the detectors to the target gases. To monitor the level of humidity and the temperature of the chamber, humidity and temperature sensors (Sensirion-SHT7x) are installed inside the chamber to record the ambient conditions. An electric fan is installed in one corner of the exposure chamber to create a uniform media for the experiments and also faster recovery of the chamber between experiments. The chamber is dried in a vacuum oven (set at 80°C) for two hours before using in the experiments.

5.1.2 Fabrication process

Gas sensor: Each of the gas detectors consists of 3D-printed parts and a metal oxide semiconductor (MOS) gas sensor (FIGARO, TGS 2602) (see Figure 5-2). The detectors can be connected to sampling chamber or lab environment via the three-way valves.

Microchannel: The details of the fabrication process are presented in Chapter 3. In essence, the microfluidic channel is coated with two different coating combinations (as it is shown in Figure 5-2): (A) Detector O includes three layers of chromium (35 nm), gold (65 nm), and
parylene C (4 μm); and (B) Detector X includes four layers of chromium (35 nm), gold (65 nm), and parylene C (4 μm), and Cytonix (100 nm). The dimensions of the channel are kept the same in both detectors: \( l = 20 \text{ mm}, w = 3 \text{ mm}, d = 500 \mu\text{m} \), where \( l \), \( w \) and \( d \) represent the channel length, width and depth, respectively.

**Channel hydrophobicity**: To show the level of hydrophobicity of the channel surface, the contact angles of a droplet of deionized water (DI water) on both fabricated channel surfaces are estimated (see examples presented in Figure 5-2C and 5-2D). Each contact angle is measured five times (using ImageJ), and the average and standard deviation were obtained. Different surface treatments (resulting in different wettability) is attributed to the polarity of the top layer coated on the channel [255].

**Figure 5-1** Schematic of the experimental setup. Two 3D-printed detectors are simultaneously connected to the exposure chamber using three-way manual valves.
Analytes: A set of experiments are performed using a number of VOCs with different polarities including: alkanes, ketones, and alcohols (which are mentioned from minimum to maximum polarity from left to right). A constant concentration (1000 ppm) of each of the analytes is injected into the system (for different experiments) using a precise micro-sampler (Pipet-Lite XLS). The concentration of the analyte is kept constant during all the experiments to eliminate the effect of the change in the analyte concentration on the detector response curves.

Table 5-1 lists the properties of the analytes tested here [256]. All the properties are related to each other. For example, as the hydrocarbon chain becomes larger in alcohols the molar mass increases, and on the other hand, the diffusion coefficient and vapor pressure both decrease.
Also, the larger the hydrocarbon chain the lower the polarity of the compound. This will result in having a smaller relative polarity number and larger boiling point. Similar trends are also seen among the ketone and alkanes.

**Table 5-1** List of analytes tested here with their physical and chemical properties [256].

<table>
<thead>
<tr>
<th>Gas</th>
<th>Formula</th>
<th>Molar Mass [g/mol]</th>
<th>Diffusion Coefficient [cm²/s]</th>
<th>Vapor Pressure (20°C) [mmHg]</th>
<th>Relative polarity</th>
<th>Boiling point [°C] at 20°C</th>
<th>( \gamma_{LV} ) at 20°C in N/m</th>
<th>( \gamma_{LV} ) at 20°C in mN/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>32.04</td>
<td>0.1520</td>
<td>97.66</td>
<td>0.762</td>
<td>64.6</td>
<td>7</td>
<td>16.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>46.07</td>
<td>0.1181</td>
<td>44.62</td>
<td>0.654</td>
<td>78.5</td>
<td>4.6</td>
<td>17.5</td>
</tr>
<tr>
<td>1-propanol</td>
<td>C₃H₇OH</td>
<td>60.1</td>
<td>0.0993</td>
<td>21.00</td>
<td>0.617</td>
<td>97.0</td>
<td>2.9</td>
<td>20.8</td>
</tr>
<tr>
<td>2-pentanol</td>
<td>C₅H₁₁OH</td>
<td>88.15</td>
<td>0.071</td>
<td>6.03</td>
<td>0.488</td>
<td>119.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>58.08</td>
<td>0.1049</td>
<td>180.01</td>
<td>0.355</td>
<td>56.2</td>
<td>3.1</td>
<td>22.1</td>
</tr>
<tr>
<td>Pentane</td>
<td>C₅H₁₂</td>
<td>72.15</td>
<td>0.0856</td>
<td>429.78</td>
<td>0.009</td>
<td>36.1</td>
<td>0</td>
<td>16.2</td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td>86.18</td>
<td>0.0732</td>
<td>120.00</td>
<td>0.009</td>
<td>69.0</td>
<td>0</td>
<td>18.4</td>
</tr>
</tbody>
</table>

After six minutes, the sample is completely evaporated and uniformly spread into the chamber. The two detectors are then exposed (using the three-way valves) to the exposure chamber for 40 sec. The gas molecules start diffusing into the dead-end valves through the valves and reach the sensing pallets of the two sensors, which are placed at the other end of the channels. Finally, the detectors are connected to their original positions where they are exposed to the clean air again and the gas molecules diffuse out from the channels (i.e., referred to as the recovery stage). The kinetic responses of the gas diffusion along the channels are recorded (using an Arduino microcontroller) till \( t = 150 \) sec. This is long enough for the sensor to be recovered. The experiments are all carried out at the room temperature of 25±1°C and relative humidity of 30±5%. These conditions are kept constant during the experiments.

### 5.2 Results and Discussion

In this section, the transient responses recorded using the two fabricated detectors (X and O) are presented (Section 5.2.1). A feature extraction method is then applied to the transient responses to compare selectivity of the two detectors using the Euclidean distances of features in the feature space. Following the characterization of channel coating and its
polarity for each of the detectors (Section 5.2.2), the interaction between the analyte and the surface of the microchannel is quantified based on the surface free energy of the detector channel surfaces (Section 5.2.3).

5.2.1 Sensor response and selectivity

The temporal responses obtained from the sensors are normalized between 0 to 1 (for ease of comparison). The results are shown in Figure 5-3A and 5-3C for Detectors O and X, respectively. Each experiment is repeated 8 times. For each detector, the response curves show that diffusion-physisorption procedure and accordingly the slopes of the curves during exposure and recovery change as the target gas changes. As it can be seen from Figure 5-3A and C, these slopes are steeper for polar gases (e.g. methanol) as compared to non-polar gases (e.g. hexane). Also, The Detector X’s normalized responses are more distinct compared to Detector O.

To better visualize the selectivity capability of the detectors, a feature extraction method (described in Chapter 4 [60]) is used to demonstrate the results in a 3D feature space. Three different features are extracted from each normalized transient response: including: 1) $S_1$: the time at which the normalized response level reaches 0.05; 2) $S_2$: the time at which the normalized response level reaches 0.95; and 3) $S_3$: the magnitude of the normalized response at the final read out. The extracted feature vectors obtained from each set of transient responses are shown in Figure 5-3B and 5-3D for Detectors O and X, respectively. The results shown in Figure 5-3 demonstrate segregated clusters of feature vectors, representing the separation capability of the two detectors among different analytes. It is observed from the feature spaces (Figure 5-3B and 5-3D) that Detector X (coated with Cytonix) has a better separation capability as the clusters are concentrated with less overlap. To compare quantitatively the selectivity of the two detectors (O and X) among different analytes, the 3D Euclidean distances of the average feature vectors (the mean of each feature components for each analyte) are calculated for each pair of the examined analytes in the feature space using Equation (19):

$$D = \sqrt{(\text{Avg } S_{1i} - \text{Avg } S_{1j})^2 + (\text{Avg } S_{2i} - \text{Avg } S_{2j})^2 + (\text{Avg } S_{3i} - \text{Avg } S_{3j})^2}$$  \hspace{1cm} (19)

In above equation, $i, j = a, b, c, d, e, f, \text{ or } g$, refer to methanol, ethanol, 1-propanol, 2-pentanol, acetone, pentane, and hexane, respectively. The distances resulted from the interaction of each pair of analytes (from seven examined analytes) are listed in Tables 5-2
and 5-3 for Detectors O and X, respectively. As it is can be seen in Figure 5-3B, the ethanol cluster shows some overlaps with the acetone cluster in the case of Detector O. This is also confirmed from the related number to the ethanol-acetone pair in Table 5-2, where the mean distance is small (2.91) which shows less selectivity compared to the same element for the ethanol-acetone pair in Table 5-3 (for Detector X) which is 4.23. This is ~45 % more than that obtained for Detector O. The largest mean distance in both tables is for the methanol-hexane pairs which is attributed to the difference in their relative polarity numbers (listed in Table 5-1). In essence, methanol is the most polar and hexane is the non-polar analyte tested among all the tested analytes. Moreover, the average of numbers listed in Table 5-3 for Detector X is 12.45 which is ~43% more than the average of the mean distance listed in Table 5-2 for Detector O (8.70).
The normalized transient responses of Detector O (Fig. A) and Detector X (Fig. C) to 1000 ppm of methanol (green), ethanol (red), 1-propanol (cyan), 2-pentanol (magenta), acetone (blue), pentane (orange), and hexane (black). Each experiment is repeated 8 times. The feature space presentation for the seven examined analytes tested with Detector O (Fig. B) and Detector X (Fig. D).

Figure 5-3
Table 5-2 The Euclidean distances between the average feature vectors in the feature space for Detector O (coated with Cr, Au, and Parylene C). The average of all Euclidean distances in this table is 8.70.

<table>
<thead>
<tr>
<th></th>
<th>a: X</th>
<th>b: O</th>
<th>c: △</th>
<th>d: □</th>
<th>e: ▽</th>
<th>f: ⊥</th>
<th>g: *</th>
</tr>
</thead>
<tbody>
<tr>
<td>a:</td>
<td>0.00</td>
<td>4.65</td>
<td>9.12</td>
<td>15.94</td>
<td>7.81</td>
<td>14.36</td>
<td>24.91</td>
</tr>
<tr>
<td>b:</td>
<td>4.65</td>
<td>0.00</td>
<td>4.45</td>
<td>11.29</td>
<td>2.91</td>
<td>10.00</td>
<td>20.62</td>
</tr>
<tr>
<td>c:</td>
<td>9.12</td>
<td>4.45</td>
<td>0.00</td>
<td>6.83</td>
<td>1.34</td>
<td>5.89</td>
<td>16.42</td>
</tr>
<tr>
<td>d:</td>
<td>15.94</td>
<td>11.29</td>
<td>6.83</td>
<td>0.00</td>
<td>8.13</td>
<td>3.34</td>
<td>10.37</td>
</tr>
<tr>
<td>e:</td>
<td>7.81</td>
<td>2.91</td>
<td>1.34</td>
<td>8.13</td>
<td>0.00</td>
<td>6.81</td>
<td>17.42</td>
</tr>
<tr>
<td>f:</td>
<td>14.36</td>
<td>10.00</td>
<td>5.89</td>
<td>3.34</td>
<td>6.81</td>
<td>0.00</td>
<td>10.62</td>
</tr>
<tr>
<td>g:</td>
<td>24.91</td>
<td>20.62</td>
<td>16.42</td>
<td>10.37</td>
<td>17.42</td>
<td>10.62</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 5-3 The Euclidean distances between the average feature vectors in the feature space for Detector X (coated with Cr, Au, Parylene C, and Cytonix). The average of all Euclidean distances in this table is 12.45.

<table>
<thead>
<tr>
<th></th>
<th>a: X</th>
<th>b: O</th>
<th>c: △</th>
<th>d: □</th>
<th>e: ▽</th>
<th>f: ⊥</th>
<th>g: *</th>
</tr>
</thead>
<tbody>
<tr>
<td>a:</td>
<td>0.00</td>
<td>8.78</td>
<td>11.00</td>
<td>25.33</td>
<td>10.12</td>
<td>22.09</td>
<td>28.92</td>
</tr>
<tr>
<td>b:</td>
<td>8.78</td>
<td>0.00</td>
<td>10.82</td>
<td>23.25</td>
<td>4.23</td>
<td>21.42</td>
<td>28.64</td>
</tr>
<tr>
<td>c:</td>
<td>11.00</td>
<td>10.82</td>
<td>0.00</td>
<td>14.33</td>
<td>1.38</td>
<td>11.35</td>
<td>18.45</td>
</tr>
<tr>
<td>d:</td>
<td>25.33</td>
<td>23.25</td>
<td>14.33</td>
<td>0.00</td>
<td>15.26</td>
<td>4.53</td>
<td>7.12</td>
</tr>
<tr>
<td>e:</td>
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<td>1.38</td>
<td>15.26</td>
<td>0.00</td>
<td>12.00</td>
<td>18.96</td>
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<tr>
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<td>22.09</td>
<td>21.42</td>
<td>11.35</td>
<td>4.53</td>
<td>12.00</td>
<td>0.00</td>
<td>7.22</td>
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<tr>
<td>g:</td>
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<td>28.64</td>
<td>18.45</td>
<td>7.12</td>
<td>18.96</td>
<td>7.22</td>
<td>0.00</td>
</tr>
</tbody>
</table>

5.2.2 Effects of channel coating and analyte polarity

After comparing Detectors O and X in terms of their selectivity between different analytes, it is also valuable to see how changing the polarity of the coating layer influences the temporal responses of the sensor to polar and non-polar analytes. In other words, the normalized temporal responses of two sensors to the same target gas are compared to see the effect of the channel and analyte polarities and their interaction (dipole-dipole interaction between the analyte and channel surface). The normalized transient responses of the two detectors to polar and non-polar analytes are shown in Figure 5-4A and 5-4B, respectively. The extracted features from each normalized response for Detectors O and X are presented in Figure 5-4C.

As it can be seen from Figure 5-4C, the order of feature vectors in the feature space changes by moving from polar analytes to non-polar ones for the two detectors. This can also be seen in the temporal responses (Figure 5-4C). Detector O (with higher polarity) shows less resistance to non-polar analytes compared to Detector X (see Figure 5-4A). For instance, it
can be seen in Figure 5-4A that diffuse-in and -out processes for methanol happen slightly faster in Detector X with less polarity (shown with green dash line) compared to the slopes of diffuse-in and -out process for Detector O with higher polarity (shown with the green solid lines). On the other hand, for non-polar analytes such as hexane, this order changes in the temporal responses of the two detectors, where Detector O with higher polarity (e.g. the black solid line for hexane) shows faster diffusion-in and -out and eventually faster retention time compared to Detector X with less polarity of the channel surface material (e.g. the black dash line for hexane). This is due to “like dissolves like” principle: the channel surface with higher polarity (Detector O) shows a higher adsorption rate of the polar gases; whereas the channel with lower polarity (Detector X) shows a higher adsorption rate of the non-polar analytes. As a result, if polarity of the channel coating material and compound are similar, the retention time increases (physisorption increases), as the compound interacts stronger with the channel surface. Therefore, polar compounds have long retention times on polar channels and shorter retention times on non-polar channels.

Changing the channel coating from Detector O to X (more polar to less polar) has insignificant effects on polar analytes, especially on the ones with a smaller hydro-carbon chain and higher polarity. Among the four tested alcohols, 2-pentanol (the least polar alcohol) shows the largest difference in the temporal responses of the two sensors (see Figure 5-4A), which means changing the channel polarity affects the polar analytes less. On the other hand, the two detectors respond differently to less polar gases such as acetone and non-polar alkanes (e.g. pentane and hexane) (see Figure 5-4B). This has also been projected in the feature space, where the feature vectors of Detector O (presented with O markers) and the feature vectors of Detector X (presented with X markers) and their 3D Euclidean distances are shown. As it can be seen, the distances between the feature vectors of the two detectors in response to the non-polar gases are larger (e.g. 6.89 for hexane) as compared to the polar ones (e.g. 0.61 for ethanol). Therefore, the results presented in Figure 5-4 show larger differences between the two fabricated detectors in response to the non-polar gases as compared to the polar ones. This is attributed to the higher diffusion coefficient of polar gases (Table 5-1) which makes the diffusion part of diffusion-physisorption to be more effective. In other words, for the polar gases, diffusion is the dominant term in the diffusion-physisorption equation which makes the effect of channel coating (which has more influence
on adsorption) less significant. On the other hand, the non-polar gases with lower diffusion coefficients have more time to interact with the channel surfaces, and hence, are more influenced with the channel surface material.

Although the diffusion rate of different gases is a significant parameter in the device discrimination ability to distinguish different analytes, it is not the only parameter involved. As an example, ethanol and acetone have similar diffusion coefficients (~0.11 \( \text{cm}^2/\text{s} \)). Therefore, if the diffusion rate was the only parameter for discriminating these two gases, the two detectors should have shown the same response against these two gases and fail to distinguish between them. However, as it can be seen from Figure 5-3, Detectors O and X can distinguish between these two gases. Moreover, as it can be seen from Figure 5-4, the two detectors show a more significant difference against acetone (1.97) rather than ethanol (0.61). This is also related to their polarity and the fact that changing the channel coating has more influence on less polar gases (such as acetone) rather than polar ones (such as ethanol). This is an obvious indication of the fact that the analyte discrimination in microfluidic gas detectors is not a purely diffusion-based process, and there are analyte/channel surface-related parameters involved in enhancing/impeding sensor selectivity. As indicated in Figure 5-4C, the difference between the feature vectors of 2-pentanol is 3.9, which is the largest among all the other alcohols and it is even higher than some of the less polar gases (such as acetone for which the difference between the feature vectors is 1.97). Comparing the diffusion coefficient of these two gases also justifies these numbers: acetone has a higher diffusion rate than 2-pentanol. In the next section, the surface free energy of the two fabricated channels (Detectors O and X) are estimated to quantify the interaction between the analyte and channel coating and its relation to the sensor discrimination power.
Figure 5-4 (A) The normalized transient responses of Detector O (solid lines) and Detector X (dash lines) to 1000 ppm of methanol (green), ethanol (red), 1-propanol (cyan), 2-pentanol (magenta). (B) The normalized transient responses of Detector O (solid lines) and detector X (dash lines) to 1000 ppm of acetone (blue), pentane (orange), hexane (black). (C) The feature space presentation for Detector O (shown with O markers) and Detector X (shown with X markers) for 7 tested analytes.
5.2.3 Channel surface free energy

To determine the channel surface free energy of the two fabricated detectors, the Owens, Wendt, Rabel and Kaelble (OWRK) method [257] is used. The contact angle values of five of the tested analytes (methanol, ethanol, acetone, pentane, and hexane (as the representatives of the three families of alcohol, ketone and alkane)) on the channel surface of the two fabricated detectors are measured and listed in Table 5-4. The values represent the average of five measurements, and the error presents the standard deviation.

Table 5-4 The contact angle measurement of five analytes on the surfaces of both detectors. The angles listed here are the averages of five measurements and the error represents the standard deviation. The liquid-vapor and solid-vapor measured for both detectors are also listed here (the method of calculation of these values are explained at the end of this section).

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Contact angle on Detector O channel surface</th>
<th>Contact angle on Detector X channel surface</th>
<th>$\gamma_{SL}$ for Detector O</th>
<th>$\gamma_{SL}$ for Detector X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>$13^\circ\pm2$</td>
<td>$46^\circ\pm3$</td>
<td>$0.28\pm0.07$</td>
<td>$0.85\pm0.10$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$16^\circ\pm2$</td>
<td>$48^\circ\pm2$</td>
<td>$2.07\pm0.1$</td>
<td>$2.67\pm0.09$</td>
</tr>
<tr>
<td>Acetone</td>
<td>$5^\circ\pm1$</td>
<td>$46^\circ\pm3$</td>
<td>$1.37\pm0.06$</td>
<td>$0.09\pm0.10$</td>
</tr>
<tr>
<td>Pentane</td>
<td>$10^\circ\pm2$</td>
<td>$17^\circ\pm1$</td>
<td>$5.11\pm0.09$</td>
<td>$2.07\pm0.06$</td>
</tr>
<tr>
<td>Hexane</td>
<td>$8^\circ\pm1$</td>
<td>$16^\circ\pm1$</td>
<td>$7.45\pm0.06$</td>
<td>$0.08\pm0.05$</td>
</tr>
</tbody>
</table>

Based on the OWRK method, each of the interfacial tensions (liquid-vapor ($\gamma_{LV}$) and solid-vapor ($\gamma_{SV}$)) are broken down into two terms: polar surface tension ($\gamma^p$) and dispersive surface tension ($\gamma^d$) parts [258] (see Eq. (20) and (21)).

\[
\gamma_{LV} = \gamma^d_{LV} + \gamma^p_{LV} \quad \quad (20)
\]

\[
\gamma_{SV} = \gamma^d_{SV} + \gamma^p_{SV} \quad \quad (21)
\]

The values for polar and dispersive liquid-vapor ($\gamma_{LV}$) for the tested analytes are listed in Table 5-1. Combining Good’s and Young’s equations (Eq. (22)) and substituting Eq. (20) into it will result in Eq. (23):

\[
\begin{align*}
\gamma_{SL} &= \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma^d_{SV}\gamma^d_{LV}} - 2\sqrt{\gamma^p_{SV}\gamma^p_{LV}} \\
\gamma_{SL} &= \gamma_{SV} - \gamma_{LV} \cos \theta
\end{align*}
\quad \quad (22)
\]
This equation can be simplified to a linear equation in the form of \( y = A + Bx \), where

\[
\begin{align*}
 y &= (1 + \cos \theta) \left( \frac{(\gamma_{LV}^p + \gamma_{LV}^d)}{2\sqrt{\gamma_{LV}^d}} \right) \\
x &= \frac{\gamma_{LV}^p}{\gamma_{LV}^d} \\
A &= \sqrt{\gamma_{SV}^d} \\
B &= \sqrt{\gamma_{SV}^p}
\end{align*}
\]

After measuring the contact angles of different analytes on the both channel surfaces of Detectors O and X, the linear Eq. (23) is used to determine the solid surface tension of each of the fabricated channels. The results are shown in Figure 5-5A and 5-5B for Detectors O and X, respectively. Each O or X marker in Figure 5-5A and 5-5B presents the average value obtained from the five runs of contact angle measurements for each analyte. The error bars present the standard deviation from the average. The solid-vapor surface tension \( \gamma_{SV} \) can then be measured from Figure 5-5A and 5-5B for each particular surface. In essence, the line intercept (A) and slope (B) are the square roots of the dispersive and polar parts of the solid-vapor surface tensions, respectively. The results show that the solid-vapor surface tension \( \gamma_{SV} \) for the channel surface of Detector O (coated with Parylene C as the top layer) is 23.15 mJ/m\(^2\), and for the channel surface of Detector X (coated with Cytonix as top layer) is 17.81 mJ/m\(^2\).
Figure 5-5 Owen-Wendt method is used for the determination of the surface free energy of two different channel coating surfaces for (A) Detector O, and (B) Detector X.

Using the Young’s equation (Eq. (22)), the solid-liquid surface tensions ($\gamma_{SL}$) can then be estimated for each of channel surfaces for different analytes. These results are listed in Table 5-4. Interestingly, the differences between the values of $\gamma_{SL}$ for the two detectors’ surfaces are smaller for polar analytes (e.g. for methanol it is 0.56) and higher for non-polar analytes (e.g. for hexane it is 5.2). This was also observed in Figure 5-4C, where the feature vectors of non-polar gases showed greater Euclidean distances for the two detectors, whereas the feature vectors for polar gases for the two detectors showed smaller Euclidean distances in the feature space. Figure 5-6 shows the linear relation between the distances of the feature vectors of the two detectors (shown in Figure 5-4C) vs. the differences between $\gamma_{SL}$ for the two channel surfaces of the two detectors ($\Delta \gamma_{SL}$) for each of five tested analytes. This also shows the non-polar gases behave more differently than the polar ones as the surface of the channel changes. This is attributed to the fact that for the non-polar gases (with smaller diffusion rates) physisorption of the gas molecules to the channel walls is more dominant.
Figure 5-6 The linear relation between the Euclidean distances of the feature vectors of the two detectors vs. the difference between the surface tension of solid-liquid for the two detectors obtained for different analytes.

5.3 Summary
Two microfluidic-based gas detectors were fabricated with two different channel coating combinations (of layers) with different hydrophobicity. The selectivity of the two fabricated detectors among different analytes were compared (both qualitatively and quantitatively). It has been shown that changing the polarity of the channel coating creates a more significant effect on the position of feature vectors of non-polar gases compared to polar ones. This is attributed to the higher diffusion rates of polar gases as compared to non-polar ones. This means that for the polar gases diffusion is the dominant term in the diffusion-physisorption equation which makes the effect of channel coating (which has more influence on adsorption) less significant. On the other hand, for the non-polar gases, lower diffusion coefficients result in having more time to interact with the channel surfaces, and hence, those are more influenced with the channel surface material. The comparison between the surface tensions of both channels showed that the difference in the solid-liquid surface for non-polar analytes is greater compared to polar ones. This supports the fact that changing the polarity of the channel coating alters more significantly the position of the feature vectors for non-polar analytes. These results can be used to design an array of micro-channels with different polarities to increase the segregation power of the device.
Chapter 6  Diffusion-based humidity control membrane for microfluidic-based gas detectors

In the previous chapters, a microfluidic based gas detector is developed which works based on different molecular diffusion and also adsorption and desorption rates of the gas molecules to the channel walls. The device is able to differentiate among different gases [60]. Such a device has been characterized based on the coating materials and dimensions of the microfluidic channel [60]. In addition to the low-cost of the sensing components, calibration of such a device is much simpler than other methods presented in Chapter 1. The only problem associated with such a device is its vulnerability to ambient fluctuations such as humidity and temperature [227]; the responses of a typical sensor to the same concentration of an analyte in different ambient conditions are different [259]. Such deficiency is detrimental; for example, in breath analysis applications, any small fluctuations in humidity can result in false positive or negative results, causing irreparable consequences. As a result, a study has been performed on the effects of the temperature and humidity fluctuations on the sensor response and performance. Controlling the temperature of the system can simply be done using a proportional–integral–derivative controller (PID controller). The effect of temperature on the performance of the gas detector is studied and presented in Chapter 7 (as one of the applications of the device in detection of THC, which is the psychoactive part of cannabis). It is shown in Chapter 7 that controlling the temperature of the channel can improve the sensing capability of the device in detecting big molecules (such as THC). However, any humidity changes have a negative impact on the sensor response as it declines the sensor signal by weakening the diffusion process of gas molecules (see below). Therefore, a humidity control system is required to regulate the level of humidity.

In this chapter, the effect of the level of relative humidity on the response of a microfluidic-based gas analyzer is studied. A low-cost and reliable humidity control membrane for microfluidic gas detectors is developed. The developed humidity control system contains a membrane which is placed at the interface of the sampling and exposure chambers. This humidity control membrane lowers the humidity of the sample gas and also stabilizes the

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Parts of this chapter have been submitted as a full paper to Sensors and Actuators B: Chemical.
humidity using inexpensive inorganic salts. Thus, two experimental setups are designed: (i) to study of the effect of humidity on the sensor response (with no humidity removal element), and (ii) to remove/minimize the effect of humidity on the sensor response using a humidity control membrane. Using the first experimental setup, the microfluidic-based gas sensor is tested against four gases (ethanol, methanol, 2-pentanol, and 2-pentanone) in different humidity levels ranging from 15%-80%. The results show that in the presence of humidity the device fails to not only differentiate between different gases, but also cannot identify different concentrations of one gas. Using the humidity control system (the second experimental setup) the humidity level of the gas chamber is lowered and kept at a certain value. Then, the transient responses of the sensor in different humidity levels are recorded. It is shown that the humidity control membrane eliminates the effect of humidity on the sensor response.

6.1 Experimental Method

6.1.1 Experimental setup for studying the effect of RH

This experimental setup consists of four major parts (see Figure 6-1A): an enclosed 3D-printed gas chamber for sample injection (sampling chamber), an enclosed 3D-printed gas chamber for exposure of the detector to the gas (exposure chamber), a 3D-printed diffusion-based membrane at the interface of the two gas chambers for the humidity removal purpose, the 3D-printed gas sensor (installed on the exposure chamber using a screw hinge). The two chambers each with a volume of 100 cm³ are 3D printed in one piece (similar to the one explained in Chapter 3), and are fully sealed to prevent leakage of the gas molecules and humidity. One of the chambers (sampling chamber) is used as the humidity control container (and also gas sample injection container) and the other one (exposure chamber) is used to expose the sensor to the target gas. To monitor the level of humidity and the temperature of the chambers, humidity and temperature sensors (Sensirion-SHT7x) are installed inside each chamber to record the ambient condition. An electric fan is installed in the exposure chamber to make a uniform media for the experiments and also faster recovery of the chambers between experiments. Both chambers are dried in a vacuum oven (set at 80°C) for two hours before they are used in the experiments. The procedure for studying the effects of relative humidity (RH) on the sensor is as follows: similar to the study conducted by Greenspan and et al. [260], a variety of inorganic salts are used to create different and constant RH values in
a sealed cylindrical container (the salt container). The salts chosen here include KOH (15%), MgCl\(_2\) (33%), NaBr (55%), NaCl (73%), and K\(_2\)SO\(_4\) (80%). The values in the parenthesis represent the ultimate relative humidity that can be achieved using the above mentioned salt solution. The salts are used to create different RH in the system and to stabilize the level of humidity. Three grams of each of the inorganic salts is mixed with appropriate content of de-ionized (DI) water into the salt container and placed in the corner of the sampling chamber through the inlet, which is placed on the top face of the chamber. The 3D-printed gas sensor, which consists of two parts and a MOS gas sensor (FIS, SP3-AQ2), is mounted on top of the exposure chamber (see Figure 6-1B). The sensor can rotate over the chamber using a screw hinge (the details of sensor fabrication are reported in [60]: the microfluidic channel is coated with layers of chromium (35 nm), gold (65 nm), and parylene C (4 \(\mu\)m), and the dimensions of the channel is \(l = 20\) mm, \(w = 3\) mm, \(d = 500\) \(\mu\)m, where \(l\), \(w\) and \(d\) represent the channel length, width and depth, respectively).

**Figure 6-1** (A) The schematic of the experimental setup. The sensor is mounted on the 3D-printed chambers. The sensor can rotate over the exposure chamber (exposure stage), and can rotate back to the clean air for recovery. (B) the schematic view of the 3D-printed sensor.
After the RH level of the container reaches an equilibrium state, different concentrations of each of the analytes is injected into the system (for different experiments) using a precise microsampler (Pipet-Lite XLS). After six minutes, the sample is evaporated and uniformly spread into the chambers. In these series of experiments, the exposure and humidity control chambers are connected via a 3D-printed part (in between two chambers) which contains no humidity removal element at this stage. The sensor is then rotated around the hinge and exposed to the exposure chamber for 30 sec., after which the humidity level of this chamber is reached a desired level. A small through hole is made on the top plate of the exposure chamber in a way that when the sensor is rotated over its hinge and placed on top of the chamber the sensor inlet is aligned with the chamber outlet, so the gas diffuses into the channel. The gas molecules diffuse into the dead-end channel and reach the sensing pallet of the sensor, which is placed at the other end of the channel. Finally, the sensor is rotated back to its original position where it is exposed to the clean air again and the gas molecules diffuse out from the channel in the recovery stage. The kinetic responses of the gas diffusion along the channel are recorded (using a microprocessor) till $t = 100$ sec (which is long enough for the sensor to be recovered). The device remains in this position for a few minutes before the sensor becomes fully recovered and ready for the next experiment. The regular atmosphere of the laboratory is the background media for all the experiments. The experiments are all carried out at a room temperature of $25\pm 1^\circ C$.

6.1.2 Experimental Setup with a humidity removal membrane

A 3D-printed humidity removal membrane is developed in order to eliminate the effect of the humidity on the response of the sensor. The membrane consists of three major parts: 3D-printed frame with through holes (two pieces), a non-woven polypropylene fabric (two pieces), and the KOH salt (which can reduce RH more than any other salts listed above). The 3D-printed parts work as a frame which holds everything in place. The non-woven polypropylene fabric repels the fluid back because of its low surface energy and hydrophobicity. The image of the 3D-printed chambers and humidity membrane (also the schematic of different components of the membrane) are shown in Figure 6-2.

The KOH salt of 20 g was mixed with DI water and used as the main part of the humidity removal membrane. The membrane is placed at the interface of the chambers enabling diffusion of the gas molecules through the membrane and spreading into the exposure
The humidity of the sampling chamber is varied (using the salts listed in Section 6.1.1) in the range of 15%-80% for different experiments. The membrane decreases the humidity to 15% (±3%). Therefore, the sensor is exposed to the same humidity in all the experiments.

**Figure 6-2** (A) The image of the 3D-printed chambers. (B) Different parts of the humidity removal membrane, which contains three major parts: 3D-printed frame, non-woven polypropylene fabric, and salt. The frame is 3D-printed with matrix of through holes.

### 6.2 Results and Discussion

#### 6.2.1 Effect of humidity

The responses of the sensor to a range of different concentrations (1000-4000 ppm) of four gases (ethanol, methanol, 2-pentanol, and 2-pentanone) were measured at four different
relative humidity levels including 15%, 35%, 55%, and 80% (each with ± 3% fluctuation). For different humidity levels, the level of response of the sensor is different. A feature extraction method is used for characterization of different analytes at different humidity levels. Three different features are extracted from each transient response (see Figure 6-3A). The three extracted features from each transient response include: 1) the slope of the line approximating the diffuse-in segment of the signal \( F_1 \), 2) the absolute value of the slope of the line approximating the diffuse-out segment of the signal \( F_2 \), and 3) the surface area underneath the response curve \( F_3 \). The feature vector \( \varnothing \) extracted from the transient response is shown in a 3D space in Figure 6-3B. It has been suggested \[60\] that the three selected features present the analyte and humidity related information, as humidity changes the diffusion procedure and accordingly the slope of the lines approximating the diffuse-in and out segments of the response.

Figure 6-3 (A) a typical transient response of the sensor to a concentration of a gas at certain humidity. (B) The feature extraction method used for identification of the humidity of the analyte is presented. Three selected features are the maximum level of the transient response \( F_1 \), the response level at the final readout \( F_2 \), and the area under the transient response curve \( F_3 \).
The transient responses of the sensor (with the coating layers and dimensions reported in [60]) to a range of different concentrations of ethanol (1000-4000 ppm) are shown in Figure 6-4A, C, E, and G at different humidity levels: 15%, 33%, 55%, and 80%, respectively. The feature vectors related to each set of experiments are shown in Figure 6-4B, D, F, and H. The results show separated feature vectors, representing the separation capability of the device among different concentrations of the same analyte at each humidity level. It is observed that for higher levels of humidity the response has a smaller magnitude, which means in higher levels of humidity smaller amounts of gas molecules diffuse into the channel. In addition, the gases tested here (alcohols) are all polar, mostly hydrophilic, and tend to attract water molecules. Therefore, these molecules are adsorbed in the humid environment of the chamber. As a result, an increase in the humidity level of the test chamber impedes the transient response of the sensor.

**Figure 6-4** The transient responses of the sensor to ethanol with different concentrations (1000-4000 ppm), at different humidity levels: 15% (A), 33% (C), 55% (E), 80% (G). The feature space of the sensor to ethanol with different concentrations at different humidity levels: 15% (B), 33% (D), 55% (F), 80% (H).
Figure 6-5A shows the transient responses of the sensor to different concentrations (1000-4000 ppm) of ethanol in 4 different humidity levels (15%-80% all in one figure). As it can be seen, if the humidity of the chamber and the analyte concentration both fluctuate, the sensor alone will not be able to segregate different features from the response profile. In other words, all of the feature vectors associated with each concentration of the analyte at different humidity levels overlap in the feature space (see Figure 6-5B). Thus, the device fails to differentiate between different concentrations or humidity levels, and there will be errors in the feature extraction and segregation method. Similar experiments were conducted for other VOCs (at 1000 ppm) in different humidity levels (ranging from 15% to 80%) and the transient responses are shown in Figure 6-6A. As the humidity increases the response levels of one gas decrease (see Figure 6-6A).

**Figure 6-5** (A) The transient response of the sensor to a range of concentrations (1000-4000 ppm) of ethanol at different humidity levels. (B) The feature space presentation for (A).
As described in [60], a specific feature extraction method can be used to differentiate different VOCs with respect to their type and not their concentration. Since in this case, the type of the gas is the goal of the pattern recognition, and the analytes are classified in the feature space based on their categories not their concentrations. Therefore, using a normalization method [60], the response level is normalized between 0 to 1, with the intention of eliminating the effect of humidity on the response level. This type of feature extraction includes [60]: (a) $S_1$, the time at which the normalized response level reaches 0.05, (b) $S_2$, the time at which the normalized response level reaches 0.95, and (c) $S_3$, the magnitude of the normalized response at the final read out. Thus, the 3D feature space coordinate is defined based on $S_1$, $S_2$, and $S_3$, where each response is depicted as a point ($S_1$, $S_2$, $S_3$). Figures 6-6B and C show the normalized responses and the 3D feature space, respectively. As it can be seen, the normalized response profiles of some of gases overlap. These overlaps are even more obvious in the 3D feature space (see Figure 6-6C). These overlaps are due to the failure of the feature extraction method, resulting in the loss and misplacement of useful features. Thus, the feature extraction itself is not enough to eliminate the effect of humidity on the response level.
Figure 6-6 (A) The transient responses of the sensor to 1000 ppm of ethanol (red), methanol (green), 2-pentanol (blue), and 2-pentanone (black) at different RH levels (tested in the range of 15-80%). (B) The normalized transient responses of the sensor to 1000 ppm of four VOCs at different RH levels. (C) The feature space presentation for the normalized responses shown in (A).
To compare quantitatively the selectivity of the device in the presence and absence of the humidity fluctuation, the 3D distances of the average feature vectors (mean of the feature components for each analyte) are measured for each two different analytes in the feature space using Eq. (26).

\[ D = \sqrt{(\text{Avg } S_{1i} - \text{Avg } S_{1j})^2 + (\text{Avg } S_{2i} - \text{Avg } S_{2j})^2 + (\text{Avg } S_{3i} - \text{Avg } S_{3j})^2} \quad , \ i,j = a,b,c,\text{or } d \] (26)

in which \(a, b, c, \text{or } d\) refer to 2-pentanol, 2-pentanone, methanol and ethanol, respectively. These values are listed in Table 6-1. The element listed in this table is the result of the interaction of the components of each pair of four different analytes. As it can be seen in the Table 6-1, the mean distances are small which shows failure of selectivity of the used feature extraction method (e.g., the mean distance between ethanol and methanol in the feature space is only 1.97 which confirms the overlap of their features in the feature space). The largest mean distance is for ethanol and 2-pentanol (8.49) which is attributed to the larger difference in their chemical properties (compared to ethanol and methanol). The mean distance between 2-pentanone and 2-pentanol is also small (1.57) which is also attributed to their related chemical compounds. 2-pentanone has the largest numbers in the table since it is the only ketone in the list.

<table>
<thead>
<tr>
<th></th>
<th>a:</th>
<th>b:</th>
<th>c:</th>
<th>d:</th>
</tr>
</thead>
<tbody>
<tr>
<td>a:</td>
<td>0.00</td>
<td>1.59</td>
<td>6.78</td>
<td>8.49</td>
</tr>
<tr>
<td>b:</td>
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<td>0.00</td>
<td>5.31</td>
<td>6.94</td>
</tr>
<tr>
<td>c:</td>
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<tr>
<td>d:</td>
<td>8.49</td>
<td>6.94</td>
<td>1.97</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Table 6-1** The distances between the average feature vectors in the feature space at different RH levels.

### 6.2.2 Effect of humidity removal membrane

In the previous section, it was shown that the effect of humidity cannot be eliminated using just feature extraction and post processing of the sensor response; therefore, a humidity removal membrane is used here to practically eliminate this effect on the device response. The humidity removal membrane shown in Section 6.1.2 is used to stabilize the humidity of the exposure chamber to a desired level (in this case KOH is used, as it can lower the humidity level and enhance the response of the sensor more than any other slats). Experiments are repeated using the humidity removal membrane between the sampling
chamber and exposure chamber. As the gas goes through the humidity removal membrane, the humidity of the gas is lowered, and hence the humidity effect on the response is eliminated. The humidity of the exposure chamber is measured to be 15%, 5 minutes after sample injection in the chamber (right before starting the experiment). Figure 6-7A shows the transient responses of the sensors at different humidity levels (ranging from 15% to 80%) created in the humidity control chamber (the sampling chamber) for four different VOCs. As it can be seen from the response profile of each gas, all the transient responses (for different humidity levels in the humidity control chamber) have the same pattern and almost the same amplitude which is due to decreased humidity in the exposure chamber. In essence, the humidity membrane lowers the humidity of the exposure chamber as well as the sampling chamber over time so that the entire system reaches the same humidity (e.g., in the case of using KOH aqueous solution the humidity control system stabilizes the humidity of both chambers at 15±3%). The normalized responses and 3D feature space for all the humidity levels and four VOCs are shown in Fig 6-7B and 6-7C, respectively. It is shown that the VOCs are successfully segregated in four different clear-cut clusters in the feature space. Again, Eq. (26) is used to find the distances of the average feature vectors (see Table 6-2). The distances are increased by 36% compared to those listed in Table 1 which proves that the humidity removal membrane increases the selectivity of the device among different VOCs.

Table 6-2 The distances between the average feature vectors in the feature space with controlled RH.

<table>
<thead>
<tr>
<th></th>
<th>a:</th>
<th>b:</th>
<th>c:</th>
<th>d:</th>
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</thead>
<tbody>
<tr>
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<td>7.16</td>
<td>9.43</td>
</tr>
<tr>
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<td>2.23</td>
<td>0.00</td>
<td>9.38</td>
<td>11.66</td>
</tr>
<tr>
<td>c:</td>
<td>7.16</td>
<td>9.38</td>
<td>0.00</td>
<td>2.28</td>
</tr>
<tr>
<td>d:</td>
<td>9.43</td>
<td>11.66</td>
<td>2.28</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Figure 6-7 (A) The transient responses of the sensor to 1000 ppm of ethanol (red), methanol (green), 2-pentanol (blue), and 2-pentanone (black) at different RH levels in the range of 15-80% using the humidity control membrane (controlled humidity at 15%). (B) The normalized transient responses of the sensor. (C) The feature space presentation for normalized responses shown in (B).
6.3 Summary

A low-cost and reliable humidity control system was developed to eliminate the effect of humidity on a microfluidic-based gas analyzer device. The developed device reduces the level of humidity and also stabilizes it using inorganic salts. The microfluidic-based gas sensor is first tested against four different gases in different humidity levels ranging from 15%-80%. The results of the study of the effect of humidity fluctuation on the sensor showed that the sensor is vulnerable to humidity and the humidity effect cannot be eliminated using only post processing and feature extraction techniques. Using the humidity membrane, the humidity of the gas chamber is controlled at 15%, and the transient responses of the sensor in different humidity shown that the proposed humidity control system significantly enhances the selectivity of the device.
Chapter 7 Applications

As it is mentioned in Chapter 1, gas analyzers have variety of applications including: food and beverage quality assessment, medical diagnostic and monitoring devices, and safety and environmental monitoring. Here, three major applications of the proposed gas detector are presented. The proposed gas detection system can detect VOCs from both liquid or gas samples. In Section 7.1, an application of the device for liquid sample detection is introduced. The device includes a MOS sensor integrated into a digital microfluidic (DMF) platform to manipulate, analyze and identify different wine samples. DMF platforms have been extensively developed for liquid sample preparation [261-262], as they are reliable and scalable devices for creating and transporting small droplets on an array of planar electrodes [263-264]. Here, DMF chips are coupled with the diffusion-based gas sensor for rapid recognition of wine aromas (section 7.1). The developed device can successfully differentiate between seven different wines from different manufacturers and different vintage years. In section 7.2, applications of the proposed gas analysis technique in detection of gaseous samples is presented. In section 7.2.1, a highly selective multi target gas detector is developed for the purpose of detection of biomarkers in breath. The developed device is used for detecting binary and triple mixtures of different biomarker gases. Another application of the proposed gas detector is presented in Section 7.2.2: detection of THC for potential detection of cannabis in the breath. Since Tetrahydrocannabinol (THC) is a relative big molecule with low diffusion rate, the microchannel of the gas detector is heated using a heater to amplify the diffusion coefficient of the analyte molecules. The device is calibrated based on standard methanol-THC solutions and pure methanol to see the effects of THC molecules on the sensor response. The humidity of the device is controlled using a two-step humidity control filtering system using: Zeolite powder (as the first filter to lower the humidity) and KOH salt (as the second filter to lower and also stabilize the humidity). In Section 7.2.3, another application of the proposed gas detection technique in pinpointing pipeline leakage is presented. A specific configuration of the device is presented which has the ability to be installed on a drone and to be sent over the infrastructure and find the

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6 Parts of this chapter have been published as a full paper in IEEE Sensors.
potential leakage location. Due to the novel configuration of the device, it has the ability to flush the examined gases out the sensor which is due to the outlet and solenoid valve added to the design. This sensor recovery method automatically regenerates the saturated sensors using a compressed air recovery chamber and electrically actuated solenoid valves in order to continuously monitor the infrastructure for leakage detection. For the proof of concept, the device is calibrated against pentane.

7.1 Application of the proposed gas detector in detection of liquid samples

On-chip electronic nose for wine tasting: A digital microfluidic approach

Throughout history, wine has spread through many civilizations across the globe due to its diverse texture and flavor. Wine is more than a beverage, as societies manifest their cultural identities through their unique vines and fermentation techniques. To elevate their fermenting technique, wineries rely on the delicate and extraordinary palette of their winemakers.

With the recent growth in the wine industry, wineries are in the search of automated and precise methods of wine characterization to achieve the required repeatability. These methods provide a powerful tool for winemakers to quantitatively verify the standards of production, uniformity within a brand, and to avoid product misrepresentation [265]. Therefore, there is an emerging demand for simple, rapid, and cost-effective technologies for quality assessment of wines.

The chemical composition of wine is typically defined by the method of preparation and the primary products used for its production [265]. Wine is one of the most complex alcoholic beverages. While ethanol and water are the main components of wine, numerous volatile and non-volatile compounds, including polyols, fatty acids, esters, aldehydes, ketones, lactones and cyanins are also present in small quantities [266]. While all of these compounds contribute to the unique taste of wine, it is the VOCs that particularly yield the complex aroma of wine. Therefore, characterizing the VOCs in wine can mimic the assessment of wine aroma by an expert wine winemaker to identify key features of wine.

To develop quantitative methods for wine characterization, numerous methods have been developed including gas GC [267] and MS [268]. GC/MS have long been used for the analysis of food and beverage samples. However, these bulky devices are expensive and time consuming. Artificial nose [269-271] and taste [272] sensors, (also called “electronic nose” (e-nose) and “electronic tongue” (e-tongue)) are feasible alternatives to mimic the human
nose and palette (as explained in Chapter 1). As for the sensory part of the e-noses and e-tongues, several sensors have been developed including optical, colorimetric, and piezoelectric-based sensors [269, 273]. However, the independent drifts and the large number of array components (sensors) results in cumbersome recalibration and frequent replacements of expensive parts [274-275-15]. Therefore, there is an urgent need for an alternative detection technology. In this thesis, the microfluidic gas detection device is used to characterize different wine samples. As it is mentioned before, VOC gas molecules have different diffusion and adsorption/desorption in the microfluidic channel, which results in a unique kinetic response of the sensor upon exposure to a gas mixture. After an extensive calibration, these diffusion-based gas sensors are suitable for determining each component of any VOC gas mixture including wine aroma.

To use the diffusion-based single sensor for wine aroma characterization, a controlled volume of a wine droplet must be exposed to the inlet of the micro-channel. Therefore, an automated system is needed to produce the desired volumes of wine from a reservoir. A gas sensor is integrated into a DMF platform for analysis of liquid samples (wine droplets). For this purpose, a MOS gas sensor is integrated into an open DMF system for detection of VOCs in the wine aroma. The effect of water cross-sensitivity of the gas sensor is eliminated using a hydrophobic porous micro-channel, which provides selective detection of wine droplet aromas. The transient responses of the device to the diffused aroma of seven different wines (three different types of Shiraz, Cabernet, Syrah, Sauvignon Blanc, and Shiraz/Cabernet blend) along the channel are recorded and compared. It is shown that device successfully differentiate among different wines with the same ethanol concentration. In the following paragraphs, the experimental setup, fabrication procedure, and results and discussions are presented.

As shown in Figure 7-1, an on-chip gas sensor consists of three parts: 1) a DMF chip to facilitate extraction and manipulation of small droplets of wine; 2) a diffusion channel to provide selectivity among different gases in wine aroma and to remove the water cross-sensitivity of the sensor; and 3) a general-purpose MOS gas sensor integrated for the detection of the different wine aromas.
Figure 7-1 The schematic of the digital microfluidic diffusion channel-based wine detection device.

DMF systems can be designed based on two different configurations [276]: (i) single plate DMF also referred to as open DMF systems, in which the droplet is exposed to the environment and it is actuated on an array of electrodes, and (ii) double plate DMF also called closed DMF systems in which the droplet is confined between two parallel plates. Each platform has its own advantages. For instance, it is easier to access the droplet in the open system, while the closed system minimizes droplet evaporation, and facilitates droplet splitting on the chip [276]. A novel device for pumping a column of liquid in a microchannel integrated on DMF platform is presented in Appendix I. In this method, a column of liquid is manipulated indirectly using another actuation droplet in a form of digital micro pump. The above-mentioned method prevents applying direct high voltage to the target sample and reduces sample degradation.

Despite the flexibility of the closed system, in this application (wine tasting) accessibility of the reservoir in the open system is preferred over controllability and portability of the closed system. Here, we have used DMF for wine sample manipulation toward a continuous
microfluidic channel used for segregation of the VOCs in the wine. For the sample extraction and manipulation, an open DMF chip was fabricated as follows: a glass slide was used as the substrate and it was coated with 65-nm gold (Au) and 35 nm Chromium (Cr) under the gold layer for adhesion using Physical Vapor Deposition (PVD) sputtering machine (Angstrom Engineering, Nexdep deposition system). A series of electrodes were patterned on the gold-coated glass substrate through photolithography process using positive photoresist (Microposit S1805 positive photo resist, A016FBI001). A 4-μm layer of Parylene C was then coated on the chip as a dielectric layer (using a Chemical Vapor Deposition (CVD) Parylene C coating machine, model: SCS. PDS 2010 Labcoater). To make the DMF surface hydrophobic and facilitate droplet motion, a thin layer of Teflon was coated on the chip using spin coating technique (1500 rpm for 40 s). The actuation circuit for the DMF platform is consisted of an AC signal generator (Tektronix AFG3021B) and a voltage amplifier (Tabor Electronics high-voltage wideband amplifier 9400). An AC square wave signal with the frequency of 1 kHz and an amplitude in the range of 200 Vp-p was applied for manipulation of the wine droplets on the array of gold electrodes.

The aroma diffusion part is made of a 3D-printed channel (with the depth of 500 μm) which has been sputtered with Cr and Au and coated with Parylene C (the same as the procedure mentioned for the DMF chip). These layers have been shown to be optimum coating composition for the gas diffusion channel (see Chapter 4). Finally, the surface was coated with Teflon to provide hydrophobicity and prevent sample penetration into the channel.

The gas detection part is made by integration of a general-purpose MOS gas sensor (Figaro, TGS2602) onto four gold electrodes (see Figure 7-2). The sensor is made of a chemoresistor and a microheater fabricated on the sides of an alumina substrate. To integrate the sensor on the DMF chip, the sensor is removed from the casing and then installed on the gold electrodes using a conductive silver paste. The sensor is then isolated from the environment using a 3D-printed chamber which is glued to the glass substrate (as shown in Figure 7-2A). The only path for the gas molecules to reach the sensing pallet of the sensor is the microchannel. During the experiment the inlet of the channel is exposed to the wine droplet. This method of isolation can be further enhanced by using closed DMF systems in which there is less exposure to the environment. Of course, the environmental noise can be further minimized by a better prototyping and packaging of the proposed device.
Figure 7-2 (A) The digital microfluidic platform integrated with the diffusion-based on-chip gas sensor. (B) MOS gas sensor integrated on the DMF chip.

Using an interface circuit (including a microcontroller) the output signal of the sensor is converted to digital data that is fed to a computer. The bias circuit for gas sensor is a 5V DC voltage for the microheater and a voltage divider circuit to read the voltage across the sensing pallet of the sensor (which is in series with a constant resistance).

The experiments are all carried out at the room temperature of 25±1°C and the laboratory relative humidity level of 40±5%. These conditions are kept consistent during the experiments. To extend the capability of the device to be able to use it in outside laboratory conditions as well, temperature and humidity control hardware systems are suggested to avoid ambient fluctuations. Moreover, a post processing on the data and developing a model (software) for different humidity levels and environment temperature has promising values in device calibration for different weather conditions.

Wine droplet manipulation on the DMF platform and exposure to the diffusion channel is shown in Figure 7-3. The droplet is exposed to the channel inlet for 40 s (which has been found to be an optimum time) and then actuated away from the channel using the DMF
electrodes. The diffusion rate, which is impeded by adsorption of the wine gas molecules to the surface of the Teflon-coated diffusion channel, changes the concentration profile of the wine aroma (VOC vapors) along the channel (and at the sensor). While hydrophobicity of the channel prevents the droplet from blocking the channel, it facilitates the diffusion of wine aroma into the channel. For each experiment, a 10-μL droplet of wine was formed on the DMF electrodes. The sample volume is chosen to be 10 μL based on the geometry of the channel and DMF electrodes. This volume can be reduced by optimizing the dimensions of the channel and electrodes size. Using a closed DMF system, the sample volume can be further decreased. By sequentially actuating the electrodes, the droplet was manipulated and exposed to the inlet of the hydrophobic diffusion channel for 40 s (the diffuse-in process). The 40-second duration of the diffuse-in time was optimized to reduce the sensor response time while providing the sufficient selectivity. The droplet was then transported away from the inlet of the channel toward a waste reservoir and the channel was remained open for 160 s (the diffuse-out process). The 160-second diffuse-out time was optimized to enhance the selectivity and sensor recovery. The transient response of the sensor was recorded for total of 200 s (using a microcontroller).

The typical response of the sensor is shown in Figure 7-4. As the sample droplet approaches the channel inlet, the VOCs of wine diffuses into the channel, the reaction between the MOS and VOC compounds results in a change in the sensor resistance. By removing the sample from the inlet of the sensing channel the diffuse-out process starts and the sensor recovers to its baseline resistance as the oxygen concentration increases in the chamber.

The diffuse-out process is found to be slower than the diffuse-in process (see Figure 7-4), which is mainly due to the lower vapor concentration gradient along the channel. Two features were defined and extracted from the kinetic response of the sensor, representing the diffuse-in and -out processes. Before extracting the features, the time response was normalized to 0 to 1 to eliminate the effect of the concentration of the sample.
Figure 7-3 (A) Actuating the wine droplet towards the diffusion channel, (B) Exposing the channel to the wine droplet for 40 s. (C) Actuating the wine droplet away from the channel.

The method of extracting two features ($S_1$, $S_2$) from the normalized response is demonstrated in Figure 7-4. For every normalized response, the rise time ($t_r$) and peak time ($t_m$), is defined as the time needed for the response to reach 5% and 100% of the maximum value, respectively. The final time is defined as the final measurement time (which is 200 s in this study). The feature $S_1$ is defined as the slope of a line from the rise time to peak time, and $S_2$ is defined as the slope of the line from the peak time to final time.

Eight different wine samples (listed in Table 7-1) including four Shiraz from different brands and vintage, Cabernet, Syrah, Sauvignon Blanc, Shiraz/Cabernet blend were examined. Shiraz and Syrah are two red wines made from the same grape but in different areas and climates. Cabernet, which is known for its astringent tannins [277], is another red wine made
all around the world and, depending on the climate and the soil, can be grown with different flavors. Sauvignon Blanc is a popular white wine grown in different regions across the world and is renowned for the fact that it can produce interesting flavors based on the ripeness of the harvest [278].

![Figure 7-4](image)

**Figure 7-4** The typical normalized transient response of the sensor to a concentration of a gas (blue). The related line diagram (purple) specified by determining $t_r$ and $t_m$ moments where the response profile reaches 5% and 100% of its maximum level, respectively, and $R_f$, the dimensionless magnitude of the profile at $t_f$ (the last read-out time).

**Table 7-1** Different examined types of wine and their characteristics.

<table>
<thead>
<tr>
<th>Wine</th>
<th>Vintage</th>
<th>Alcohol %</th>
<th>Country</th>
<th>Manufacturer</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shiraz</td>
<td>2013</td>
<td>14.5 %</td>
<td>Australia</td>
<td>Peter Lehmann</td>
<td>red</td>
</tr>
<tr>
<td>Shiraz</td>
<td>2013</td>
<td>14.5 %</td>
<td>Australia</td>
<td>Layer Cake</td>
<td>red</td>
</tr>
<tr>
<td>Shiraz</td>
<td>2014</td>
<td>14.5 %</td>
<td>Australia</td>
<td>Layer Cake</td>
<td>red</td>
</tr>
<tr>
<td>Shiraz</td>
<td>2013</td>
<td>14.5 %</td>
<td>Australia</td>
<td>Wolf Blass</td>
<td>red</td>
</tr>
<tr>
<td>Cabernet</td>
<td>2013</td>
<td>14.5 %</td>
<td>Argentina</td>
<td>Mascota</td>
<td>red</td>
</tr>
<tr>
<td>Syrah</td>
<td>2012</td>
<td>14.5 %</td>
<td>Chile</td>
<td>Leyda</td>
<td>red</td>
</tr>
<tr>
<td>Sauvignon Blanc</td>
<td>2015</td>
<td>12.5 %</td>
<td>New-Zealand</td>
<td>Matua</td>
<td>white</td>
</tr>
<tr>
<td>Shiraz Cabernet</td>
<td>2014</td>
<td>14.5 %</td>
<td>Australia</td>
<td>Koonunga</td>
<td>blend</td>
</tr>
</tbody>
</table>
The temporal responses obtained from the device are normalized to eliminate the influence of the analyte concentration on the shape of response. Each experiment was repeated five times with different operators in different days to assure the reproducibility of the measurement. Temporal responses of the sensor to five different wines (one of the Shiraz and the other 4 types of wines) are shown in Figure 7-5A.

![Figure 7-5A](image)

**Figure 7-5 (A)** The normalized responses for five different types of wines (Shiraz, Cabernet, Syrah, Sauvignon Blanc, and Shiraz-Cabernet blend). Each experiment is repeated for five times. (B) The 2D feature vector map of five types of wine is presented. The features extracted from the normalized responses of the five types of wines are segregated in the 2D feature space.

The kinetic response of the gas sensor is sensitive to changes in humidity and temperature of the surrounding environment (as discussed in Chapter 6). The hydrophobic coatings for the diffusion channels acts as a moisture barrier and reduces the effect of humidity on the sensor.
response. The transient responses of sensor to these wines are somehow overlaying on each other. For example, the difference between the temporal responses of Shiraz and Syrah is small, which is attributed to almost identical origins of these two types of wines. However, the feature extraction method explained in the previous section can separate these responses. These two features are defined in a way to represent the diffuse-in/diffuse-out processes of the wine aroma moving into/out from the channel. The feature vectors are plotted in a 2D map shown in Figure 7-5B. Interestingly, it is shown that choosing just two features from each normalized response is adequate for differentiating these wines.

To quantitatively compare the selectivity of the device to different types of wine, the 2D Euclidean distances of the average feature vectors (the mean of the feature components for each wine) are calculated for each two different wines in the feature map using Equation (25).

$$D = \sqrt{(\text{Avg} [I/S_a] - \text{Avg} [I/S_b])^2 + (\text{Avg} [I/S_a] - \text{Avg} [I/S_b])^2}$$  \hspace{1cm} (25)

In the above relation, \(i, j = a, b, c, d, \) or \(e\) refer to Shiraz, Syrah, Sauvignon Blanc, Cabernet, or Shiraz-Cabernet, respectively. The elements listed in this table are the result of the interaction of the components of each pair of five different wines. As it can be seen in the Table 7-2, some of the mean distances are small which shows less selectivity (e.g., the mean distance between Shiraz and Syrah in the feature space is only 0.83 which confirms the overlap of their features in the feature space). Interestingly, the largest mean distances are for the pairs of Shiraz-Cabernet and pure Cabernet (36.02) and Shiraz-Cabernet and pure Shiraz (33.03) which are attributed to the difference in the chemical compound of the blend compared to that of Cabernet or Shiraz.

**Table 7-2** The Euclidean distances between the average feature vectors in the feature map for 5 types of wine (The average of all Euclidean distances in this table is 13.11).
Thus, the device successfully differentiates between five different wine samples. Going back to the example of Shiraz and Syrah, the feature map (Figure 7-5B) shows that these two types of wines can be segregated with some minor overlaps. The overlaps between Syrah and Shiraz in Figure 7-5B mainly occur due to the $S_1$ feature, which is a representative of the diffuse-in process. Therefore, the segregation between these two types of wines is attributed to their diffuse-out process. This can be related to a slower desorption rate of Syrah than that of Shiraz which results in the depletion of VOCs from the channel.

The transient responses of Shiraz, Cabernet and the Shiraz-Cabernet blend are also shown in Figure 7-5A. The $S_1$ feature for the blend is in between those of Shiraz and Cabernet, showing that the blend wine has the distinctive characteristics of both Shiraz and Cabernet wines. The results presented here show that the finger prints (“smellprint”) of different wine aromas on the sensor are distinct, proving selectivity among different wines. A better quantitative comparison can be evaluated based on calculating boundary lines in the feature map to find specific regions related to different aromas.

To study the effect of different vintage years on the identification method presented here, Shiraz wine is selected within the same brand (Layer Cake) with different vintage years (2013 and 2014). Also, Shiraz wine of two different brands, Layer Cake and Wolf Blass (both 2013), are tested and compared. The normalized temporal responses for these three types of Shiraz wines are shown in Figure 7-6A. Each experiment is repeated five times. As it can be seen in Figure 7-6B, the feature positions of two Shiraz from Layer Cake are relatively close to each other, which show the similarity in their origin. This shows the wine aroma is dependent on climate change among different years. If the weather is too hot early in the season, the grapes can ripen more quickly, which means the sugar levels and fruit flavors are ready for harvest. On the other hand, if it is a rainy and cold summer, then the grapes will fall behind in ripening, which will eventually affect the wine taste and aroma [279]. For instance, in 2014 in South Australia, the weather in spring season was cold with high rainfall. This resulted in poor harvest of the fruit, followed by a period of hot weather which caused an early vintage. In essence, red wines (especially Shiraz and Cabernet Sauvignon) were more aromatic in South Australia in that year.
(A) The normalized responses for three different types of wines (two Shiraz from the same company; Layer Cake, vintage two different years 2013 (blue) and 2014 (red), and a 2013 vintage Shiraz from Wolf Blass (black)). Each experiment is repeated for five times.

(B) The 2D feature vectors map of three types of wines. Features extracted from the normalized responses of the three types of wines are segregated in the 2D feature space.

The sample content of the alcohol can also be measured by the device. To show the ability of the device in measuring the content of ethanol of the solution a set of experiments has been performed on different ethanol and water mixture solutions ranging from 12% to 16% ethanol concentrations (which is the typical concentration range of ethanol in the wine). The transient responses of the sensor to different concentrations of ethanol in ethanol-water mixture are shown in Figure 7-7. As it can be seen in Figure 7-7, the concentration of ethanol in the solution is related to the area underneath the curve. In other words, by increasing the concentration of ethanol in the solution the area underneath the curve increases. As it was
shown in previous chapters, a feature extraction method (based on the area under the curve) can be used to find the concentration of a target gas (e.g., ethanol in this case). The transient response of the sensor to Shiraz wine is also shown in Figure 7-7 to show the difference between the response to the wine sample and the response of the sensor to ethanol-water mixture. Although, the magnitude of the peak of the response curve obtained for the Shiraz wine is similar to that of the solution with 14% ethanol concentration, their overall response curves are different. This confirms the fact that ethanol and water are not the only major components of the wine affecting the sensor response shape. The other major reported VOCs in the wine are [266]: Methyl-2-propanol-2 (7 g/L), Butanediol 2,3 (1 g/L), Methyl-3-butanol-1 (0.2 g/L) Methyl-2-propanol-1 (0.1 g/L, and methanol (0.1 g/L).

Figure 7-7 The transient responses of the sensor to ethanol-water solution samples with different concentrations of ethanol ranging from 12% to 16% (blue). The transient response of the sensor to Shiraz wine (red).

7.2 Application of the proposed gas detector in detection of gaseous samples

7.2.1 Highly selective multi target biomarker analyzer
The 3D-printed gas sensor is used for detection of biomarker gases that are potentially present in an exhaled breath. To show the diagnostic power of the developed miniaturized gas sensor, capable of differentiating small concentrations (ppm level) of different VOCs, the binary and triple mixtures of biomarker gases are tested. To maximize the device selectivity, the inner surfaces of the channel is treated with the optimum coating combination presented before. As shown in Figure 7-8, the device successfully differentiates between the
components of binary mixtures (within the range of 30-2000 ppm). The progress of the diffusion process, which is impeded by adsorption of the gas molecules to the surface of multi-layer coated channel, changes the concentration profile of the gas along the channel (and at the sensor). The normalized transient responses for different binary mixtures are shown in Figures 7-8A-C. The diffusion coefficients of different gases are listed in Table 7-3. While methanol response is faster due to the higher diffusivity, slower response of acetone is attributed to higher physical adsorption rate provided by the coating. This is highlighted in the feature extraction maps (Figure 7-8D-F) in which acetone shows higher values for the features, representing slower rates for gas diffuse-in and diffuse-out. As it can be seen in Table 7-3, the diffusion coefficients of ethanol and acetone are nearly the same. However, the device can differentiate between these two gases. This verifies the fact that the differentiation process is not only dependent on the diffusion rate, but also dependent on the physical adsorption and desorption rates of the gas molecules to the channel walls (as discussed in Chapter 5). In the case of triple mixtures, each mixture shows a unique set of features (Figure 7-9) which allows the device to determine the concentration of each component. The smallest detected concentration is 30 ppm, limited by the sample extraction device used in this study (as 0.1 μL is the minimum volume can be extracted by the device). The resolution can be improved by integrating automated or microfluidic-based sample preparation systems.
Figure 7-8 (A), (B), and (C) The normalized temporal responses, and (D), (E), and (F) three features ($F_1$, $F_2$, and $F_3$) extracted from each normalized response are mapped into a 3D space.

Table 7-3 The examined gases with their diffusivity values at room temperature (25°C) [24].

<table>
<thead>
<tr>
<th>No.</th>
<th>Gas</th>
<th>Formula</th>
<th>Diffusion Coefficient [cm²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
<td>CH₃OH</td>
<td>0.1520</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>0.1181</td>
</tr>
<tr>
<td>3</td>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>0.1049</td>
</tr>
</tbody>
</table>
Figure 7-9 Feature space presentation for paths related to three different binary mixtures and also triple mixtures. The cross sign in the middle is related to \((\text{Acetone})_x \cdot (\text{Ethanol})_y \cdot (\text{Methanol})_{1-x-y}\), where \(x=y=1/3\).

7.2.2 Diffusion-based microfluidic gas sensor for detection of THC

Detection of THC in breath has been suggested as an indicator of cannabis use [280]. However, as there are traces of other VOCs in the breath, it is important to differentiate among different gases, and pinpoint the distinct “smell print” of THC. VOCs detection in the breath is challenging mainly due to the low concentrations of the compounds and the complexity of the mixtures [281]. In the previous Chapters, it was shown that it is possible to add selectivity between different gases to the gas sensors by equipping them with microfluidic channels.

Based on molecular diffusion of different gas molecules travelling along a miniaturized channel, ample signals can be obtained for gas analysis. However, these microfluidic gas sensors are not suitable for detection of large molecule gases (such as THC) as the diffusion process is slow and takes more than few minutes. Here, a portable and cost-effective alternative is introduced for non-invasive detection of THC.

The experimental setup is shown in Figure 7-10B. The 3D-printed sensor is made using same fabrication method (mentioned before) and the channel is coated with multilayer combination of 100 nm copper and 4 µm Parylene C. To control the temperature of the diffusion channel,
a platinum heater wire is integrated along the channel (Figure 7-10A). The sensor is connected to an inlet port of a three-way digital valve. The two chambers are connected to the either of the valve outlets. The three ports of the digital valve are controlled and switched using an Arduino microcontroller. The analytes examined are THC (Sigma-Aldrich 1 mg/mL solution in methanol- analytical standard for drug analysis) and methanol. These analytes are selected to show the capability of in differentiating THC in presence of other VOCs. To make the device portable, different parts of the experimental setup including the 3D-printed sensor, valve, interface circuit, and battery are integrated into a hand-held aluminum case as shown in Figure 7-11. A LCD screen is used as the user interface and also to show the results of the tests.

The response time and selectivity of the sensor for THC-methanol binary mixture (1 mg/mL solution in methanol) and pure methanol are studied at different temperatures (25 °C, 40 °C and 80 °C). A method described in [60] is used to characterize the sensor response. The temporal responses obtained from the device are normalized to fit in the magnitude range of 0 to 1 to eliminate the influence of the analyte concentration on the shape of the responses. Features F₁ and F₂ in Figure 7-12 are the points in time at which the normalized response level reaches 5% and 95% of the maximum level, respectively, and F₃ is the magnitude of the normalized response at the final read out. The three features are defined in a way to represent the gas diffuse-in and the diffuse-out processes.

The sensor recovery time for THC-methanol mixture at 25 °C is approximately 15 minutes, and as the temperature is increased to 80 °C, the recovery time is reduced to under 3 minutes. The slow recovery which is attributed to high molecular weight of THC, however, is not observed for pure methanol. Therefore, the overall sensor response time is decreased drastically for THC detection by addition of the heater. Increasing the micro-channel temperature has another important effect: enhancing the selectivity. As can be seen in Figure 7-13, the selectivity of the device is increased at higher temperatures as bigger molecules of THC in the binary mixture are more actively involved in the diffusion process and react with the sensor. It must be noted that the observed response for the binary mixture of THC-methanol is distinct for each THC concentration, and we have successfully detected THC concentrations as low as 50 ppm.
Figure 7-10 (A) 3D-printed sensor with the embedded heater. (B) An image of the integrated sensor, chambers and integrated circuit for controlling the temperature.

Figure 7-11 Portable breath analyzer in aluminum casing with digital touch screen display.
Figure 7-12 The normalized responses of the sensor to (A) THC-methanol, and (B) pure methanol at different temperatures. The 3D feature space presentation for (C) THC-methanol and (D) pure Methanol.

Figure 7-13 (A) Typical normalized responses for two different analytes A and B; the selectivity factor is defined to examine the differentiation power of the sensor. (B) The sensor response time and selectivity factor between binary mixture of THC-methanol and methanol vs. channel temperature.
7.2.3 Portable microfluidic gas monitoring for leakage detection along pipelines

The Canada underground natural gas and liquids pipeline, including gathering, transmission system, and delivery, is estimated to be more than 800 thousand kilometers [282]. Maintaining the reliability and integrity of this system is in high demand as leaks can occasionally result in explosions, posing safety risks for those living and working nearby [283]. Moreover, methane which is the primary component of the natural gas is one of the most serious greenhouse gases (GHG) contributing irreversible climate change [284-285]. There are varieties of methods that can detect leakage along natural gas pipeline, range from manual inspection using trained dogs to advanced satellite based imaging [286]. The various methods include optical devices, acoustic monitoring, soil monitoring, flow monitoring, and gas sampling [286]. However, majority of these methods are expensive, and they cannot pinpoint the leakage location. Moreover, these methods are not sensitive enough to detect small gas leakage and they typically have high rate of false alarms. Therefore, rapid, sensitive and high precision leakage detector systems are critical to ensure the security of the natural gas infrastructure.

Here, a highly selective, portable, and fully automated gas analyzer for continuous monitoring of pipeline for drone applications is presented. To show the detection power of the developed gas detector, a simulated trial test demonstration is developed using a pipeline which leaks controlled concentrations of pentane gas into the environment. The main advantage of the proposed device over current gas detection techniques is the new configuration of the microfluidic gas sensor which enables selective gas diffusion for a range of different gases (which might exist in the background air) which is attributed to the microfluidic channel [60], and also flushing the examined gases out the sensor which is due to the outlet and solenoid valve added to the design. This novel sensor recovery method automatically regenerates the saturated sensors using a compressed air recovery chamber and electrically actuated solenoid valves in order to continuously monitor the infrastructure for leakage detection. The schematic of the experimental setup is shown in Figure 7-14.
Figure 7-14 (A) Schematic view of the experimental setup. (B) Image of the fabricated device, suitable for integration on UAV. (C) The 3D printed gas sensor equipped with inlet and outlet. (D) The device is mounted for field tests.

The sensor is lightweight and has a small footprint. Therefore, it can be mounted onto an unmanned aerial vehicle (UAV) and sent along the pipeline. With all the electronics, the total weight will be less than 1Kg. The sensor (FIGARO TGS 2610) is integrated with a 3D-
printed microfluidic-channel. The inlet of the diffusion channel is connected to the surrounding air and also to the compressed air chamber through a three-way solenoid valve (SMC VT307-6G-01N). The sensor chamber has an exhaust so the sensor can be flushed after each experiment. The connection of the sensor to the exhaust is controlled with another solenoid valve. The proposed novel configuration of the sensor allows the sensor to be recovered with clean air after each experiment and to be reused for continuous monitoring of infrastructure. To show the capability of the device, small concentrations of pentane is released into the air through a micro injector. The sensor communication with the computer is done through an XBee wireless module.

A typical response of the device to a certain concentration of pentane is shown in Figure 7-15. The progress of the diffusion process, which is impeded by adsorption of the gas molecules to the surface of channel, changes the concentration profile of the gas along the channel (and at the sensor). The typical response shown in Figure 7-15 consists of: transient phase (baseline), exposure to pentane for 10 minutes, flushing the sensor and channel with clean air for 8 seconds and finally recovery to the baseline.

![Figure 7-15 A typical response of the gas detector to certain concentration of pentane.](image)

The transient responses of the sensor to different concentrations (100-600 ppm) of pentane are shown in Figure 7-16. As it can be seen as the concentration of pentane increases the response level becomes higher. A feature extraction method is used to relate each response time to the concentration of pentane. The slope of the “exposure to pentane” which is a representative of gas concentration is chosen as the main feature of the response. This unique
feature extraction allows the device to determine the concentration of the analyte. The calibration curve of the device shown in Figure 7-17 presents the slope feature extracted from each response time against the concentration of the examined gas. Each experiment is repeated 5 times. The smallest detected concentration remains 100 ppm, which is defined by limitations of the sample extraction device used in this study (as this is the minimum volume that the pipette can collect as sample). The developed low-cost, portable and highly selective gas sensor provides a powerful tool for numerous applications including monitoring of gas pipelines and infrastructure.

![Graph showing transient responses of the device to four different concentrations](image)

**Figure 7-16** Transient responses of the device to four different concentrations (100-600 ppm).

![Graph showing calibration curve](image)

**Figure 7-17** Calibration curve for defining the concentration of pentane. The relation between the concentration and the median of the slopes of the exposure section of the curves is linear. Each marker is the median of 5 points and the error bars present the deviation from the average.
Chapter 8 Conclusions and future work

8.1 Summary

The focus of this research has been on the development of highly selective multi-target gas detection systems on microfluidics platforms to enhance miniaturized selective gas analysis methods. Integration of MOS gas sensor into a microfluidic channel and monitoring the diffusion of gas molecules in such device show potentials for identification of different volatile organic compounds (VOCs) in different applications. The low cost, portability and high selectivity are among unique features of the proposed technology.

This thesis has focused on three technical aspects (i.e., characterization of microchannel coating and geometry, quantification of the interaction between the analytes and microchannel surface, and fabrication of a humidity control system) and wide range of applications for the proposed microfluidic-based gas detectors. A summary of these aspects and results from the applications are presented below:

- A thorough study was conducted to identify an optimum channel coating and geometry, the combination of which provides high selectivity in differentiating a range of different VOCs (as compared to previous microfluidic-based gas detectors [27]). The proposed gas detector also shows a faster recovery time (150 seconds) compared to those obtained by systems presented in previous studies (15 minutes) [27]. The innovative sensing technology proposed here will advance the state-of-the-art gas analysis methods by providing real-time sensing with higher selectivity and drastically decreased recovery time. Different coating combinations were tested and compared in terms of their selectivity and recovery time. The best coating combination was suggested to be chromium, gold and parylene C. The device channel dimensions were also characterized in a way to get maximum selectivity and minimum recovery time for the device. Considering the trade-off between selectivity and the recovery time of the sensor the optimum dimension of the channel were $l=30 \text{ mm length}$, $d=200 \mu\text{m depth}$ of the channel.

- Another study has been performed on the effects of channel coating hydrophobicity and analyte polarity in microfluidic-based gas detectors. Two detectors with two different channel surface coating combinations (resulting in different hydrophobicity) were fabricated and tested against seven analytes with different polarities (methanol, ethanol, 1-
propanol, 2-pentanol, acetone, pentane, and hexane). A study on a combined feature space presentation (for both detectors) revealed the Euclidean distances between the feature vectors of the two sensors are greater for non-polar gases compared to the polar ones. Similarly, a study on the surface free energy (followed by contact angle measurement and Young’s equation) for each fabricated channel showed that the differences between solid-liquid surface tension values for the two channel surfaces are higher in the case of non-polar analytes (compared to polar analytes). This is attributed to lower diffusion coefficients for non-polar analytes which signifies the effect of channel surface adsorption in diffusion-physisorption process and eventually changes the configuration of the detector response and feature vectors. In essence, the analyte diffusion along the channel towards the sensor (placed at the end of a dead-end channel) for non-polar gases is hindered more (compared to polar analytes) by the adsorption of the analyte molecules to the channel surface. This shows that polarity of the target gas and the choice of channel coating material have significant effects on the sensor discrimination capability for different analytes.

- To eliminate the effect of humidity on the sensor response, a cost-effective and reliable diffusion-based humidity removal membrane for the microfluidic-based gas detector was developed. The developed humidity control device was shown to reduce the relative humidity (to 15% regardless the original relative humidity level) of a gas chamber and also stabilize humidity using inexpensive inorganic salts. In essence, without the humidity control device, the sensor failed to differentiate between different VOCs or even between different concentrations of the same gas when there is a slight change (as small as 5%) in humidity. The selectivity of the sensor with and without the use of the humidity removal membrane has shown to be 36% more in the case of utilizing the humidity removal membrane. The proposed humidity control system is crucial in many applications such as detection of target VOCs using breath analyzers.

- The proposed microfluidic gas detector was applied to three different applications ranging from wine characterization, to monitoring THC in air samples, to leakage detection along the pipeline. For the wine analysis, a metal oxide semiconductor gas sensor was integrated into an open digital microfluidic (DMF) system. The resulted showed that the proposed system is capable to differentiate between seven kinds of wines and their manufacturers
and vintage years. Another potential application of the proposed technology is detection of the cannabis use in human breath. A breath analyzer device is developed by integrating a wire wound heater around the sensor microchannel. The device was calibrated and shown to be highly selective towards the detection of THC in the air samples filled with THC-methanol standard solutions. Finally, the proposed technology was used to detect heavy hydrocarbons (in the gaseous form) for identification of pipeline leakage along the natural gas infrastructures. The proposed gas detector was calibrated with pentane and leakage field tests has been performed on the device. The developed leakage detector includes a novel regeneration method allowing the sensor to be recovered with clean air after each experiment and to be reused for continuous monitoring of infrastructure.

8.2 Contributions to the field
The specific contributions of this research are summarized below; each of the developments mentioned here can significantly benefit the field of gas analysis.

- A 3D-printed microfluidic platform is fabricated by integrating a chemoresistor into a microfluidic channel providing a powerful tool for analyzing the kinetic response of the device to the diffused gas along the channel. Optimum channel dimension and surface coating were determined experimentally and through studying the effect of analyte/channel surface interaction. This resulted in the development of a procedure that can be used to find the most effective channel surface material for a particular target gas.

- Another main contribution of this thesis is the control of humidity using hardware (rather than post processing the data which may not be a true reflection of the drift due to humidity). The proposed humidity control system can maintain the humidity at a low level at which its effect on the sensor becomes negligible. The concept of the proposed humidity control system can be adjusted to different applications regardless of the gas of interest.

- The major feature of the proposed technology developed in this thesis is the versatility of the gas detector. The system can be used for detection of VOCs both in liquid and gas phases and has the capability to detect a target gas in a multi-component gas mixture.
8.3 Future work

- A thorough study must be conducted to determine the effect of temperature on the sensor response and selectivity (similar to what was conducted for humidity in this thesis). Methods such as such the deep learning model [287] is recommended as they can mathematically predict the response of the sensor in different ambient conditions. Without such models, the sensor needs to be calibrated for different ambient conditions and a big data set needs to be created in order to compare the sensor response to all the recorded data (each time) to identify the type of the gas, and its concentration. This requires a large number of experiments (conducted for each target gas and the multiple combinations of different gases) and handling a large set of data (for feature extraction) which are very difficult, if not impossible.

- Different feature extraction methods are used to identify the type of the analyte and determine the concentration of the examined gas. In each feature extraction method, three (or two) features are selected from each normalized or transient response and mapped into a 3D (or 2D) feature space. It is recommended more complex feature extraction methods (such as PCA and LDA) to be utilized for obtaining more features from the transient responses of the sensor.

- Diffusion-based methods are time consuming as diffusion is a passive and slow process. One of the main challenges in adaptation of the proposed technology in real-time applications (such as pipeline leakage detection) is the long recovery time of the sensors which is currently around few minutes. For real-time detection applications (and perhaps those involving a moving vehicles), the recovery time of these sensors must be reduced. Therefore, a new configuration of the proposed microfluidic-based gas detector must be explored to facilitate sensing of gas molecules which are delivered based on advection (rather than diffusion). For instance, a gas purging system can be developed to reduce particularly the recovery time. Different microfluidic valves (including elastic polymeric membranes with piezoelectric actuators) can be integrated for an effective purging system. Finally, different dimensions of channels and gas flow rates can be examined to optimize the design for better recovery.
The application of the gas detection technique was shown for the case of breath analysis. This research needed an Ethics Approval in order to be able to work with human subjects, which was obtained towards the end of the PhD study presented in this thesis. Thus, the results presented are based on synthesized breath samples made by mixing some VOCs and increasing the humidity using different salt solutions. To prove the capability of the proposed technology as a breath analyzer, it is recommended to perform tests on human breath samples and characterize the device using different human subjects with different conditions (including: fasting, before and after eating different foods, after brushing teeth, drinking coffee, smoking cigarette and etc.).
Appendix I Development of a Digital Micropump with Controlled Flow Rate

A novel device for pumping a column of liquid in a microchannel integrated on DMF platform is presented. Electrowetting on dielectric (EWOD) method is used to frequently actuate a droplet (referred to as piston droplet) on an array of electrodes. A column of liquid (referred to as the pumped droplet) is pumped in a microfluidic channel by the pressure coming from actuation of the piston droplet. A signal modulation technique is developed and used in order to control the flow rate of the liquid column in the microchannel. Different flow rates of the pumped liquid were achieved by controlling the actuation time of the signal used for actuation the piston droplet.

I.1 Methodology

The schematic diagram of the experimental setup is depicted in Figure I1A. A signal generator is used to create an AC square wave signal. A voltage amplifier is used to amplify the output of the signal generator. The high voltage signal from the amplifier output is then sent to an interface circuit designed to switch the signal on and off by the operator. The modulated high-voltage output signal from the interface circuit is used to drive the DMF platform. The details of the interface circuit are shown in Figure I1B.

I.2 Fabrication Process

The integration of a microfluidic channel on a DMF platform is achieved by two different methods. In the first method, a series of electrodes on a copper-coated glass substrate is patterned using the S1805 positive photoresist and standard photolithography technique (see Figure I2). Each of electrodes has a surface area of 1.5 mm × 1.5 mm. To create the sidewalls of the channel, the SU8 negative photoresist is spin coated on the chip and then the mask with a straight-channel pattern is aligned on the chip and exposed to the UV light. The process is followed by developing the SU8 layer in the developer solution. The S1813 positive photoresist is then spin coated on the chip as a dielectric layer. An ITO glass is used as the top plate. To make the device hydrophobic, both bottom and top plates are coated by a thin layer of Teflon. The top plate is utilized for sealing the channel and providing the ground electrode for the DMF electrodes. The channel height using this method is around 100 µm.
To create a microchannel with a larger depth, another method of fabrication is introduced using a 3D-printed frame. The thickness of the frame (i.e. the gap size between the bottom and top plates) is 200 \( \mu m \), and the channel width is considered to be equal to the width of the fabricated DMF electrodes (1.5 mm). The frame is designed in a way to hold the bottom and top plates in a desired positions. The schematic of the 3D-printed frame and its final integration with the top and bottom plates are shown in Figures I3A and B, respectively. Since the 3D-printed frame deforms in the temperature above 60 °C, it was not possible to make it hydrophobic using Teflon coating. Thus, the microchannel was treated by the NeverWet\textsuperscript{TM} Repelling spray (from Rust-Oleum) to reduce droplet adhesion to the 3-D printed frame.

**I.3 Experimental procedure**

For all the experiments, two deionized (DI) water droplets with the distance of 5 mm are dispensed on the array of electrodes on the bottom plate. The top plate is placed on the top of
the droplets over either the pair of SU8 sidewalls or the 3D-printed frame. The volume of the piston droplet used for the experiments is $0.45 \mu L$. The pumped liquid volume is chosen as $0.65 \mu L$. Silicon oil is used as the filler medium to reduce friction and improve sealing of the channel. The pumped droplet is actuated with the signal coming from the designed interface circuit (Figure I1B). In essence, the actuation signal of the piston droplet is precisely controlled to create the desired transport rate for the pumped droplet. As it is shown in Figure I1, the signal coming from the amplifier output is an AC square wave. Using the interface circuit, this signal is frequently switched on and off for periods of $t_{on}$ and $t_{off}$, respectively. The interface circuit output AC signal is applied to the electrode beneath the piston droplet. This way, the droplet is manipulated for the controlled period of time ($t_{on}$).

**Figure I2** Fabrication process and integration of a SU8-based microchannel on a DMF platform.
Figure 13 (A) Schematic of the 3D-printed frame, and (B) 3D-printed microchannel integrated with the top and bottom plates. The clamps are applied to the assembly to squeeze the droplet between the bottom plate and top plates.

1.4 Theory

A theoretical model is developed to calculate the pressure generated in the microchannel by the piston droplet. The equivalent electrical circuit for droplet actuation by electrowetting on dielectric (EWOD) is shown in FigureI4. Here, $C_L$ and $R_L$ are the capacitance and the resistance of the piston droplet, respectively. $C_o$ and $C_D$ are the capacitance of the oil on the energized electrode and the capacitance of the dielectric layer, respectively.

The total impedance of the system can be calculated as

$$Z_{\text{total}} = \frac{1}{\frac{1}{R_L} + (C_o + C_L)i\omega} + \frac{1}{i\omega C_D}$$  \hspace{1cm} (I1)
where $\omega$ is the frequency of the applied field, and $i = \sqrt{-1}$. The capacitance and resistance values can be found based on physical and geometrical characteristics of the droplet and the DMF system.

\[
A = w^2
\]
\[
R_L = \frac{D \cdot d}{A}
\]
\[
C_L = \frac{\varepsilon_0 \varepsilon_L \cdot w \cdot x}{d}
\]
\[
C_D = \frac{\varepsilon_0 \varepsilon_D \cdot A}{t}
\]
\[
C_o = \frac{\varepsilon_0 \varepsilon_o \cdot (A - w \cdot x)}{d}
\]

\[(I2)\]

**Figure 14** (A) A schematic of the equivalent electrical circuit that models the droplet actuation mechanism based on the electrowetting-on-dielectric (EWOD) technique, and (B) droplet actuation on copper electrodes (top view).

In the above relations, $\rho$, $d$, and $w$ are the electrical resistivity of the droplet, the gap between the bottom and top plates (i.e., the height of the microchannel), and the width of the
electrode (or the width of the microchannel), respectively. \( \varepsilon_L \), \( \varepsilon_D \), and \( \varepsilon_O \) are the relative permittivity of the liquid droplet, the dielectric layer, and oil medium, respectively. Here, \( x \) represents the length of the portion of the energized electrode covered with the droplet (see Figure I4B).

In this study, the DI water droplet used as the piston droplet has the resistivity value of approximately \( 11 \, \text{M}\Omega \text{cm} \). Therefore, the resistance of the piston droplet can be assumed very large and Equation (I1) can be simplified to

\[
Z_{eq} = \frac{1}{i\omega C_{eq}}
\]

where \( C_{eq} \) is the equivalent capacitance of the system and can be written as

\[
C_{eq} = \frac{C_D(C_o+C_L)}{C_o+C_L+C_D}
\]

By considering Equation (I2), the equivalent capacitance of the system will be

\[
C_{eq} = \frac{\varepsilon_0 \varepsilon_D w^2 \left( \varepsilon_o w + (\varepsilon_L - \varepsilon_o) x \right)}{\varepsilon_o t w + \varepsilon_D w d + (\varepsilon_L - \varepsilon_o) t x}
\]

The energy that is stored in the system based on the equivalent capacitance of the system can be calculated as

\[
E = \frac{1}{2} C_{eq} \cdot V_{rms}^2
\]

Therefore, the derivative of the energy of the system with respect to the position of the droplet on the actuated electrode presents the electrowetting force that drives the piston droplet (see Equation (I6)).

\[
F_{electrowetting} = \frac{dE}{dx} = \frac{1}{2} V_{rms}^2 \frac{dC_{eq}}{dx}
\]

Figure I5 presents the energy stored in the system and the electrowetting (presented as the slope of the line fitted to the results) calculated based on Equation (I6) for both cases of SU8-based and 3D-printed microchannels. It is found that the energy stored in the system is
linearly proportional to the position of the droplet on the actuated electrode, and the electrowetting force applied on the piston droplet \( (dE/dx) \) is equal to 70 \( \mu N \) for the 100-\( \mu m \)-high SU8 microchannel, and 50 \( \mu N \) for 200-\( \mu m \)-high 3D-printed microchannel. The pressure generated in the microchannel by the piston droplet can be found by dividing the electrowetting force by the cross sectional area of the channel \( (d \times w) \) where \( d \) and \( w \) present the height and width of the channel, respectively. The pressure caused by actuating the pumped droplet is estimated to be 467 \( P_a \) for 100-\( \mu m \)-high SU8-based microchannel and 166.7 \( P_a \) for 200-\( \mu m \)-high 3D-printed microchannel.

![Graph showing energy stored in the system](image)

**Figure I5** The red circle and the blue square symbols show the energy stored in the system calculated from Equation (I6) for the SU8-based and the 3D-printed microchannels, respectively. The slopes of the black solid lines fitted by linear regression to each set of data present the electrowetting forces.

### I.5 Results

The pumping technique presented is tested experimentally. An AC square wave signal with the frequency of \( f = 1 \text{kHz} \) and an amplitude in the range of 100-200 \( V_{p-p} \) is applied for manipulation of the piston droplet on the array of the copper electrodes. Figure I6 presents the schematic of the setup and the procedure followed for turning the electrodes on and off to actuate the droplet back and forth in the microchannel. It is observed that the shape of the pumped droplet during pumping does not change which suggests the velocity profile of the pumped liquid is a plug-flow velocity profile.
Figure I6 (A) Schematic of the fabricated device, and (B) pumping a droplet back and forth in a microchannel integrated on a DMF platform.

Figure I7 presents the displacement of the pumped droplet as a function of the applied voltage. In essence, an increase in the actuation voltage amplifies the displacement of the droplet. However, after a certain voltage value ($150\text{ \, volts}$) the displacement of the pumped liquid becomes independent of the voltage and just dependent on the actuation period of the actuation signal ($t_{on}$) (see FigureI7). Using the described signal modulation technique, $t_{on}$ can be precisely controlled. This way, the power consumption of the entire system decreases
dramatically, as the actuation signal is only applied for a short period (it is turned off using the designed interface circuit for a long time ($t_{\text{off}}$) compared to the turned-on period ($t_{\text{on}}$)).

By applying the on/off signal frequently, the piston droplet is manipulated with nearly a constant velocity in the channel. As a result, the pumped droplet is driven in the channel with the same velocity as that of the piston droplet. The average velocity of the pumped droplet is shown in Figure I8 for three different cases in the SU8 microchannel design.

**Figure I7** Droplet average displacement vs. the voltage amplitude ($V_{\text{pp}}$). Three different $t_{\text{on}}$ were tested (shown with different symbols) for two different microchannel designs: SU8-based (red lines) and 3D-printed (blue lines) microchannels.

**Figure I8** The position of the pumped liquid using the pulse modulation technique.
Different flow rates of the pumped liquid can be achieved by precisely controlling $t_{on}$ of the applied voltage (the flow rate is equal to the cross sectional area of the microchannel multiply by the average velocity presented in Figure I8). Due to the fact that the velocity profile of the liquid after the pumped droplet is uniform (which means the plug flow is observed), the flow rate of the liquid after the pumped droplet is directly proportional to the pumped droplet velocity. As a result, a controlled flow rate of liquid in the channel is achieved by presented technique. Although the displacement of the liquid is dependent on the gap size ($d$), it is also possible to change the average flow rate of the fluid in the microchannel by changing $t_{off}$ and keeping $t_{on}$ constant (same scenario can be used for the 3D-printed design to create desired pumping flow rates).
References


