Comparative Study of Different Sensor Array Designs Involving Plasticized Polymer Coatings for BTEX Detection in Water

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Recommended Citation

Post, Nicholas, "Comparative Study of Different Sensor Array Designs Involving Plasticized Polymer Coatings for BTEX Detection in Water" (2018). *Master's Theses (2009 -)*. 477.
https://epublications.marquette.edu/theses_open/477

COMPARATIVE STUDY OF DIFFERENT SENSOR ARRAY DESIGNS INVOLVING PLASTICIZED POLYMER COATINGS FOR BTEX DETECTION IN WATER

by

NICHOLAS POST

A Thesis submitted to the Faculty of the Graduate School,
Marquette University,
in Partial Fulfillment of the Requirements for
the Degree of Master of Science (Electrical and Computer Engineering)

Milwaukee, Wisconsin

August 2018

ABSTRACT

COMPARATIVE STUDY OF DIFFERENT SENSOR ARRAY DESIGNS INVOLVING PLASTICIZED POLYMER COATINGS FOR BTEX DETECTION IN WATER

NICHOLAS POST

MARQUETTE UNIVERSITY, 2018

Detection and quantification of benzene, toluene, ethylbenzene, and xylenes (BTEX) in liquid phase is of interest because of the significant public health hazards posed by these compounds. BTEX are volatile organic compounds (VOCs) commonly used as additives in gasoline. Shear horizontal surface acoustic wave (SH-SAW) devices have shown promise in liquid phase sensing applications and is used to address this problem.

SH-SAW devices can be made chemically sensitive by depositing a polymer coating on the device surface. SH-SAW devices coated with commercially available polymers have shown modest sensitivity to BTEX compounds. However, there are few polymers which exhibit the properties necessary for BTEX sensing in water. The addition of plasticizer can reduce the glass transition temperature of the polymer, resulting in a blend which is suitable for sensor coatings. Polymer-plasticizer blend coatings have shown high sensitivity to BTEX compounds and as well as partial selectivity to those compounds. High selectivity is desired for more accurate identification and quantification of BTEX compounds, including in samples containing multiple BTEX compounds and other contaminants. Sensor arrays implemented with several appropriate coatings can be used to achieve the desired selectivity.

Nine sensor coatings have been developed and characterized for sensitivity and response time constant for BTEX compounds. Coating compositions include 2.5% PIB and 4% PECH polymer solutions and 17.5% DIOA-PS, 23% DINCH-PS, and 22%, 30%, 32%, 33.5%, and 35% DTP-PS polymer-plasticizer blends. Using combinations of these coatings, three arrays have been implemented and analyzed, each composed of five selected sensor coatings. Analysis of arrays formed entirely from polymer-plasticizer blend coatings indicate that highly sensitive and selective arrays can be formed using only these coatings. Results also show that coatings which are not partially selective to ethylbenzene and xylenes can be used to increase coating chemical diversity in arrays without negatively impacting array selectivity. Analysis of the three arrays has been applied to the implementation of a final array to further increase sensitivity and selectivity. Results show that this array has the highest selectivity to BTEX together with the highest sensitivity and coating diversity.

ACKNOWLEDGMENTS

NICHOLAS POST

There are many people whom I am grateful to for many different reasons. First and foremost, I would like to thank my research advisor Dr. Fabien Josse for his advice, support, guidance, and belief in me from the beginning of my academic career. He has continually presented me with opportunities to grow as a person and a researcher, and his guidance and support in my endeavors have made this research possible. Your belief in me has allowed me to push myself beyond what I believed myself capable of during my undergraduate career.

I would like to thank Dr. Florian Bender for his guidance and help in all aspects of my lab work and research. The time that he has put into training me in lab procedure, working with me on presentations for research meetings, and too many other aspects of my work to name here a huge reason that I have been able to succeed in graduate school. The experiences in the research labs that you have worked in, the places you have been to, and the life that you have lived have all proven to be invaluable to me.

I would like to thank the members of my thesis committee, Dr. Fabien Josse, Dr. Florian Bender, and Dr. Susan Schneider. Thank you for thoughtfully reviewing my thesis and being a part of my success here at Marquette University. The process of writing this thesis has been one of the most difficult tasks I have ever done, and the comments and criticisms you all provide for me will help me grow as a researcher and a writer.

I would like to thank all the members of our research group for being a part of the discussions in our group meetings each week and for your help in and out of the lab. Three people in particular have been instrumental in my growth and success in my time here. First, I would like to thank Laura Alderson for helping me with my transition from the undergraduate program here at Marquette to graduate school. From being my TA as a senior to the summer you spent getting me acclimated to our lab, your help was invaluable to me. Next, I would like to thank Pintu Adhikari for the training in the lab he provided me and the experiences he passed on to me. You are a true role model for me as a researcher and I am truly grateful to have spent the time I did learning from you. Finally, I would like to thank Karthick Sothivelr for the support and discussion he provided me in the lab. The discussions we had in the lab, in our group meetings, and the help and support you have offered me throughout my time at Marquette has been hugely helpful to my growth as a researcher and a person.

Finally, I would like to thank my family for their support of me in my graduate school endeavors past, present, and future. My mom and dad have supported me and loved me my entire life and have been just as supportive throughout my graduate career and the writing of my thesis and I am extremely grateful to them.

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1 INTRODUCTION AND BACKGROUND

1.1 Problem Definition and Objective of Research

BTEX (Benzene, Toluene, Ethylbenzene, Xylenes) detection is of great importance for public health. BTEX compounds are a common additive in petroleum products for meeting vapor pressure requirements [1]. Benzene is of particular concern as it is considered a carcinogen by U.S. government agencies [2]. The U.S. Environmental Protection Agency dictates strict maximum contamination limits (MCLs) for BTEX compounds in drinking water. The MCLs of BTEX compounds are 0.005 milligrams per liter (mg/L) benzene, 1 mg/L toluene, 0.7 mg/L ethylbenzene, and 10 mg/L xylenes (1 mg/L = 1 part per million, ppm) [3]. A need exists for a highly sensitive, reliable, and fast sensor for BTEX detection. A need also exists to increase selectivity of sensors for more accurate identification and quantification of BTEX compounds, especially in liquid environments. Carefully designed sensor arrays have the potential to improve or increase selectivity of a sensor platform beyond what a single sensor can achieve. The objective of this research is to analyze the sensitivity and selectivity of a number of proposed sensor arrays to BTEX compounds for more accurate identification and quantification of single analyte solutions of BTEX compounds.

1.2 Chemical Sensing Overview

A chemical sensor is defined as any sensor capable of detecting the presence and concentration of target analytes in any given environment [4]. For chemical sensing, there are many parameters of interest with two of the most important being the sensitivity and the selectivity. Those two parameters are defined below.

- Sensitivity – measure of sensor output signal to sensing parameter. For a given sensor, a proportional output response will be observed for a given input signal. In resonant-based sensing, sensitivity can be defined as $\Delta f/\Delta c$ where Δf is an output frequency shift and Δc is a change in input concentration [5]. Units of Hertz per ppm (Hz/ppm) are typical in chemical sensing applications.
- Selectivity – a sensor's ability to distinguish target measurands from non-target interferent inputs. Sensors are said to be highly selective if large output responses are observed for target measurands and small output responses or no responses are observed for non-target measurands. In chemical sensing selective sensors have high affinity for target analytes and low affinity for interferants.

1.2.1 Common Sensors Used for Chemical Sensing

A number of sensor platforms can be used for chemical sensing, as long as that platform can be designed or selected to have sensitivity to the chemicals of interest in gas or liquid phase. Several optical measurement techniques and acoustic wave devices can be used for chemical sensing.

1.2.1.1 Optical Chemical Sensing

Spectroscopic measurement techniques are highly sensitive and selective. Output signals of optical measurements typically yield wavenumber plots giving fingerprints unique to each molecule. Peak location and shape are used to identify chemical compounds and magnitude of peaks is used to quantify concentration [6]. Infrared (IR) spectroscopic techniques have shown the most promise for BTEX and hydrocarbon detection [6, 7].

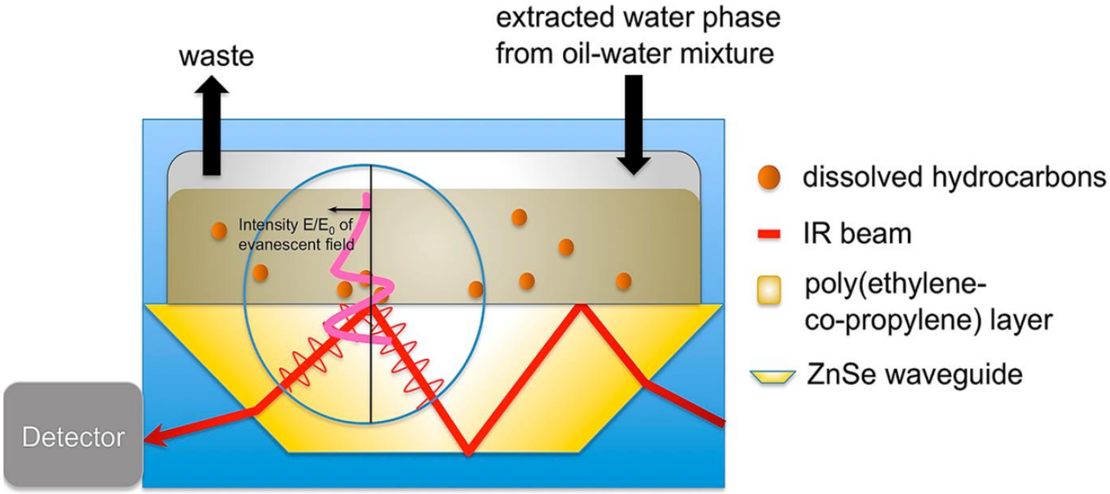

Figure 1. 1: Schematic view of measurement principle behind attenuated total reflection IR spectroscopy [6]

Shown in Figure 1.1 is a specific example of IR spectroscopy called attenuated total reflection IR spectroscopy. An infrared beam emitted from a laser propagates through a waveguide. One surface of the waveguide is coated with a polymer film. The refractive index of the polymer film changes slightly when analyte is introduced to the system, perturbing the beam. The way in which the infrared beam is perturbed allows for detection and quantification of target analytes [6].

1.2.1.2 Acoustic Wave Devices

Acoustic wave devices used as sensors utilize perturbations in acoustic wave propagation to detect and quantify input measurands. An input signal is applied to a transducer. The transducer converts the input signal into an acoustic wave which propagates through the bulk or on the surface of a substrate. The perturbed acoustic wave is converted back into an electrical output via a second transducer [8]. Piezoelectric materials are typically used as substrates for acoustic wave devices [8]. Thickness shear mode (TSM) resonators and surface acoustic wave (SAW) devices, two common acoustic wave devices used for chemical sensing, will be discussed further.

1.2.1.2.1 TSM Resonators

TSM resonators consist of a disk of piezoelectric material between two metal electrodes [9]. TSM resonators are bulk acoustic wave (BAW) devices in which a standing wave is generated between the two electrodes. At resonance, maximum displacement occurs at the device surfaces, making TSM resonators highly sensitive to changes occurring at these locations [9]. Figure 1.2 shows several views of a typical TSM resonator. A cross-sectional and top view of a resonator (left) show electrode placement and active regions of the device as described above. Also shown is acoustic wave propagation through the substrate (right), with maximum displacement at either surface. This makes the TSM resonator particularly sensitive to surface perturbations resulting in changes in the resonant frequency [9].

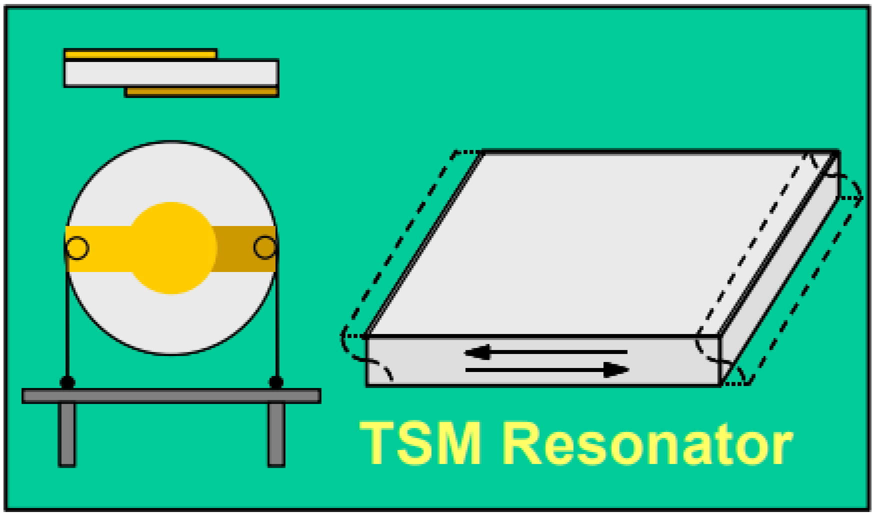

Figure 1. 2: Left: cross-sectional view (top) and top view (bottom) of a typical TSM resonator. Grey denotes substrate layer, gold denotes positive and negative electrodes. Right: Diagram showing maximum displacement of TSM resonator [9].

1.2.1.2.2 Surface Acoustic Wave Devices

SAW devices generally consist of a piezoelectric substrate with a number of interdigital transducers (IDT) patterned on its surface. To narrow this broad definition, a SAW device in a delay line configuration will be discussed. This configuration, known as a delay line configuration, consists of a piezoelectric crystal with input and output IDTs separated by a propagating path. An input voltage is provided to one IDT which generates an acoustic wave. The acoustic wave propagates along the surface of the substrate to the output IDT. The output IDT converts the mechanical acoustic wave into an output voltage [4, 9]. SAW devices are widely used in gas phase measurements but have limited application in liquid phase. This is because SAWs, also known as Rayleigh SAWs couple significant energy into the liquid layer causing high acoustic wave attenuation [11-13]. Shear-horizontal surface acoustic wave (SH-SAW) devices can be used in place of SAW devices for liquid phase sensing.

1.2.1.2.3 Shear-Horizontal Surface Acoustic Wave (SH-SAW) Devices

SH-SAW devices are suitable for liquid phase measurements because they support mostly shear horizontal particle displacement rather than compressional wave displacement. SAW devices have compressional and shear vertical wave components which couple significant acoustic energy into liquids. SH-SAW devices utilize an orientation of piezoelectric crystal substrate which only supports shear horizontal particle displacement. Liquids can support compressional waves, but not shear horizontal waves [8, 9]. Shear horizontal waves propagate slightly deeper in the substrate, which reduces device sensitivity to surface perturbations. A waveguiding layer can be deposited on the substrate surface to trap the acoustic wave more closely to the device surface. The waveguide chosen must have a lower shear wave velocity than the substrate material in order for coupling/waveguiding to occur [14]. Figure 1.3 shows a diagram of an SH-SAW device with waveguiding layer.

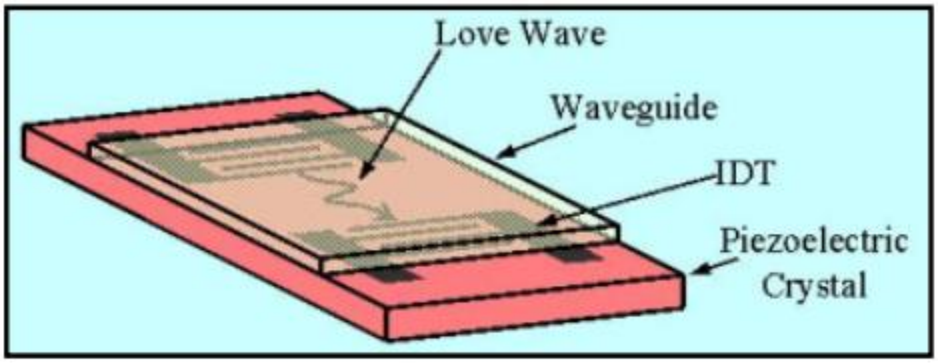

Figure 1. 3: Diagram of an SH-SAW device used as a chemical sensor with chemically sensitive waveguiding layer [9]

In some cases, the necessary waveguiding layer can also act as a sensing layer. Sensor coatings used for this work function as both a waveguiding layer and a sensing layer and will be discussed in chapter 2. This work uses SH-SAW devices as the sensing platform.

1.2.2 Polymer Coatings for SH-SAW Devices

Polymer coatings are widely used to increase sensitivity and selectivity of acoustic wave devices [4, 5, 8, 10-17]. Mechanical loading, consisting of mass loading and viscoelastic loading, is a common sensing mechanism for polymer-coated acoustic wave devices used as chemical sensors. Absorption properties of polymer coatings result in a mass loading and viscoelastic loading effects on the sensing surface of an acoustic wave device. Ideal coatings should be highly sensitive, selective, stable, have uniform thickness, and observed responses should be reversible [8]. Polymer coatings which show these characteristics are good candidates for sensing applications. This work uses several polymer-based coatings deposited on SH-SAW devices for BTEX detection.

1.3 Introduction to Selectivity and Polymer Properties

A common problem in chemical sensing is lack of sensor selectivity. Chemical identification among various compounds is important for real world implementation of sensors [17]. Limited availability of selective coatings as well as lack of good partially selective polymer candidates are significant problems in the field of chemical sensing.

1.3.1 Partial Selectivity

Partial selectivity is defined in similar fashion to selectivity. Recall that selectivity indicates high sensitivity to target measurands and low sensitivity to non-target measurands. Partial selectivity of a sensor describes how that sensor is sensitive to a number of target and non-target compounds. A partially selective sensor will have different sensitivities for each investigated target measurand even while showing some degree of sensitivity for non-target measurands. For this work, partial selectivity can indicate the analyte for which a coating is highly sensitive, less sensitive, or insensitive. Additional applications of partial selectivity exist outside the field of hydrocarbon detection, including pharmaceutical detection in liquid phase. There are a significant variety of pharmaceuticals present in drinking water [18]. Families/classes of pharmaceuticals have widely varying molecular structures. Characterizing partial selectivity of sensors for pharmaceutical detection in liquids is an emerging field of interest. This work will focus on selectivity of polymer-based coatings for SH-SAW devices to BTEX compounds.

1.3.2 Chemically Sensitive Polymers

1.3.2.1 Glass Transition Temperature

Proper selection of polymers is a key aspect of designing chemical sensor coatings. The glass transition temperature must be considered when selecting a polymer as a chemical sensor coating. The (static) glass transition temperature is defined as a range of temperatures where an amorphous polymer transitions from rubbery to glassy states [19-21]. The range of temperatures is typically simplified to one value or a small range of values, as shown in Figure 1.4.

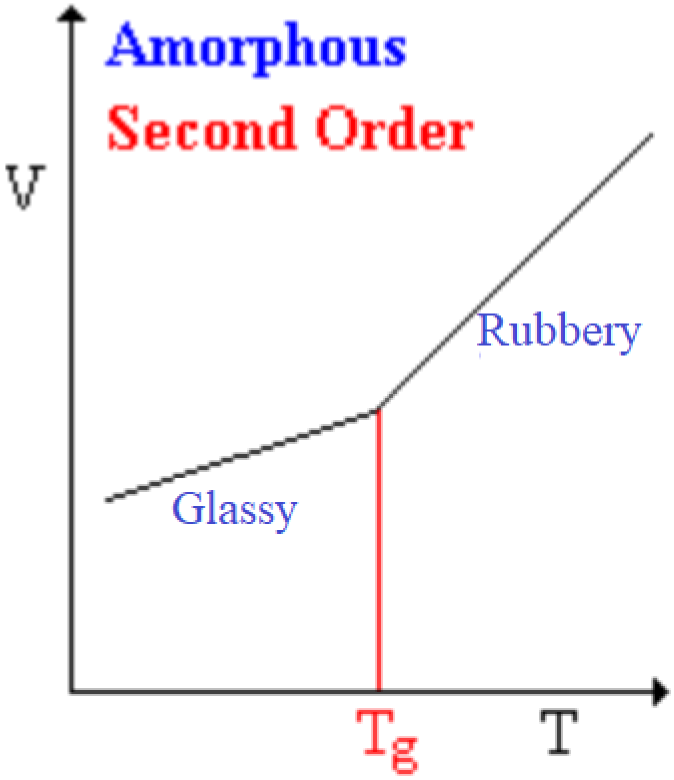

Figure 1. 4: Graphical representation of the glass transition temperature T_g as a function of temperature T and specific volume V [21]

Rubbery polymers used as chemical sensor coatings tend to exhibit higher sensitivity, faster response time, and better reversibility. Selectivity is generally low in the rubbery regime, as absorption happens more readily due to increased free volume. Glassy polymers, as chemical sensor coatings, tend to be highly selective but have lower sensitivity due to less free volume [15, 16].

1.3.2.2 Free Volume

Free volume is defined as the amount of free space between polymer molecules [19]. Increasing polymer free volume causes an increase in polymer sorption capacity. Rubbery polymers generally have more free volume than glassy polymers. Free volume increases significantly at temperatures beyond the glass transition temperature of the polymer [19]. This implies that, for high polymer free volume, it is desired to have a lower glass transition temperature (below the operational temperature of the system).

1.3.2.3 Selecting Polymers as Chemical Sensor Coatings

Polymers used as chemical sensor coatings should exhibit good sensitivity and selectivity to the target analytes. Selected polymers should also exhibit desirable response characteristics such as repeatable and reproducible responses. Ideally, selected polymers would have properties of both glassy and rubbery polymers. This criterion is very difficult to meet when selecting from commercially available polymers. Therefore, there is a need to address the lack of polymers which display the properties of both glassy and rubbery polymers needed for sensor coatings. The next two sections focus on methods of addressing this need. Sensor arrays have potential to increase selectivity by using information from several different polymer sensor coatings. Sensor coatings using specially designed polymers or polymer-plasticizer blends have the potential to increase the variety of available sensor coatings.

1.4 Sensor Arrays

Sensor arrays are groups of sensors in which each sensor contributes a unique set of data from a measured sample. Sensor arrays increase selectivity to target analytes by utilizing the unique information provided by each sensor for identification and quantification [22]. Sensor arrays have been used to increase selectivity of many sensor platforms [16, 17, 22-24]. SAW devices used as sensors have been combined to form arrays in previous works [12, 13]. In chemical sensing, proper selection of each sensor coating in the array is key to increasing selectivity. Arrays are typically paired with signal processing techniques to identify and quantify analytes [12].

1.4.1 Polymer Coatings for Sensor Arrays

Designing sensor arrays using SH-SAW devices requires selection of a diverse group of sensor coatings [12]. Coating chemical diversity implies that a variety of coatings will result in an array which is uniquely sensitive to target analytes based on the partial selectivity of the coatings. A diverse selection of polymers implies that different coatings will be more (or less) sensitive to some target analytes than other coatings and guarantees some degree of selectivity to target analytes. Careful selection of polymers based on their properties can further increase selectivity. The lack of viable polymer candidates makes polymer diversity alone insufficient for sensor array design. Signal processing techniques combined with multivariate sensing allow for more information to be gathered from each sensor response.

1.4.2 Principal Component Analysis

There are many signal processing techniques which can be used to analyze data from a wide variety of sensor platforms [23]. For this work, Principal Component Analysis (PCA) will be used to help identify the analyte present in a sample with a given sensor response. PCA extracts features of a given set of coating parameters to reduce the dimensionality of that data set [25]. The correlation or covariance matrix of the data set is created, and eigenvectors and eigenvalues are found. This information is used to reduce the order of the system and to form clusters from the reduced data set. Clusters correspond to analytes for which the array can be considered selective, provided that clusters do not overlap [25].

1.4.3 Common Problems Using Sensor Arrays

Sensor arrays and accompanying signal processing techniques are very good at identifying single analyte solutions. However, they struggle to identify and quantify binary mixtures and cannot be used for mixtures of three or more analytes [29]. Results of signal processing techniques when using only sensitivity data of sensor arrays become less accurate for increasing number of analytes. In addition, it is difficult to identify and use commercially available polymer coatings to implement sensor arrays to differentiate between analytes with similar molecular structures.

1.5 Designed Polymers and Polymer-Plasticizer Blends

To increase selectivity, several polymer-coated sensors have been proposed recently, each suitable for different applications. Discussed below are three methods for increasing selectivity of polymer coatings, which are functionalization of polymers, molecular imprinted polymers (MIPs), and plasticization of polymers.

1.5.1 Functionalized Polymers

Polymer functionalization involves adding a functional group to a polymer chain via copolymerization or other methods [11]. The specific functional group added can be selected such that it will increase polymer affinity to the target analytes. The glass transition temperature of the selected polymer is altered when functional groups are added. This and other properties can be tailored to the target analyte to increase selectivity [11].

1.5.2 Molecularly Imprinted Polymers

MIPs in chemical sensing mimic a popular technique used in biosensing applications. Receptors are specifically designed to attach to target analytes [26, 27]. A polymer is copolymerized with a placeholder molecule having a structure molecularly similar to the target analyte. The polymer is slightly crosslinked to prevent some molecular motion. Placeholder molecules are removed via chemical reaction or physical process. Remaining is a polymer molecule with a receptor having an inverse shape to that of the placeholder molecule. This structure is used as a receptor for the target analyte [26, 27].

1.5.3 Polymer-Plasticizer Blends

For hydrocarbon detection, the addition of a plasticizer to a polymer has been shown to increase sensitivity [15, 16]. Adding plasticizer to a polymer will decrease the glass transition temperature of that polymer. Enough plasticizer will make the blend behave as a rubbery polymer, yielding increased free volume in the coating [16]. Figure 1.5 shows one theory of how the addition of plasticizer effects polymer molecules.

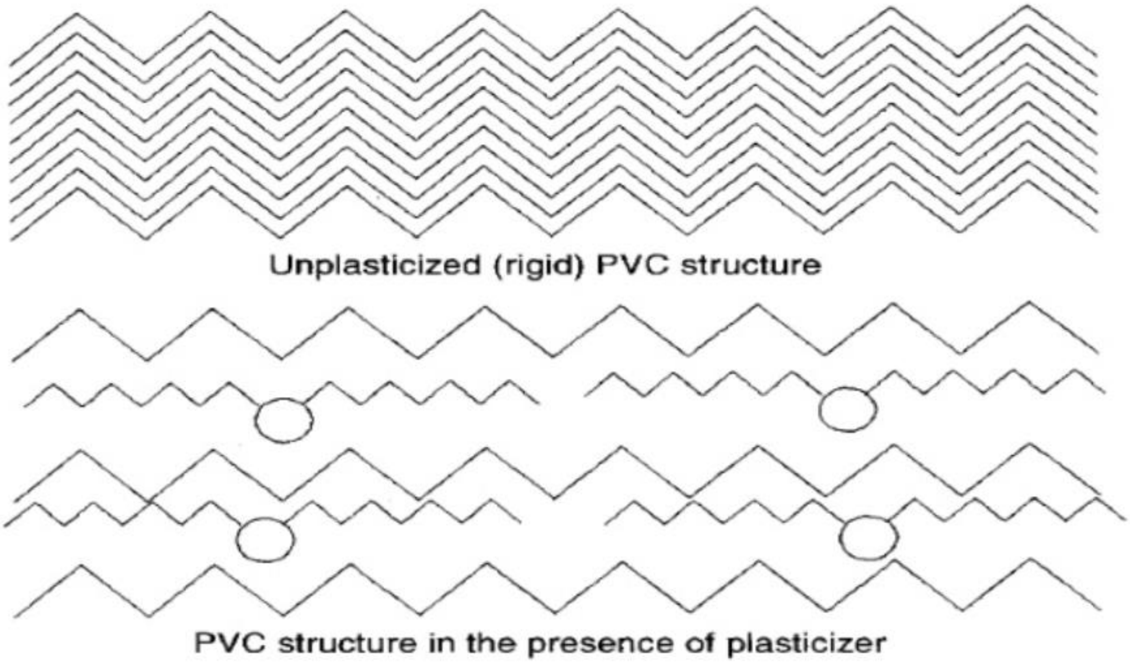

Figure 1. 5: Diagram of a polymer (Polyvinyl chloride – PVC) and the interactions between plasticizer and polymer molecules. Top: PVC molecules tightly packed together. Bottom: PVC molecules after the addition of plasticizer. [19]

Proper selection of plasticizer is equally as important as the selection of the polymer when making polymer-plasticizer blends. Factors such as compatibility play a large role in dictating the properties of the final blend. Not all plasticizers are compatible with all polymers [19]. Selecting an incompatible plasticizer for the blend can result in unstable coatings or no sensitivity to target analytes. If polymer and plasticizer are selected properly sensor coatings with high sensitivity and selectivity to target analytes can be achieved. More detailed discussions on polymer and plasticizer properties will be provided in chapter two.

1.6 Problem Statement, Objective of Research, Solution Approach

BTEX detection in liquid phase is of interest due to serious risk to human health. This need can be extended to detection of priority pharmaceuticals which present increasing risks to human health and the environment [28]. This research focuses on the design of sensor arrays for the detection of BTEX compounds in liquid phase with high sensitivity and partial selectivity.

The objective of this research is to analyze three sensor arrays consisting of SH-SAW devices coated with various polymer and polymer-plasticizer blend coatings. Arrays will be analyzed with respect to sensitivity and selectivity of the overall array for each BTEX analyte. Sensor coatings made from commercially available polymers Poly(epichlorohydrin) (PECH) and Polyisobutylene (PIB) [66] and polymer-plasticizer blends made from polymer Polystyrene (PS) and plasticizers Diisooctyl Azelate (DIOA) [37] and 1,2-Cyclohexane Dicarboxylic Acid Diisononyl Ester (DINCH) [54] have been previously designed by our research group. Coatings made with various mixing ratios of PS and plasticizer Ditridecyl Phthalate (DTP) have been designed for this work.

The three arrays to be analyzed all consist of five coated SH-SAW devices used as chemical sensors. One array will utilize only polymer-plasticizer blend coatings, with several plasticizers being used. The second array will consist entirely of polymer-plasticizer blend coatings each made from the same polymer-plasticizer pair with a varied mixing ratio. The third array will consist of both polymer-plasticizer blend coatings and coatings made from commercially available polymers.

Analysis will be performed on these arrays to achieve several specific goals. Increasing sensitivity while maintaining partial selectivity is desirable for a sensor array. Array sensitivity will be discussed to determine if the arrays presented show suitable sensitivity to BTEX compounds. It is reasonable to expect selectivity of each array to change as different coatings are being used. Differences in selectivity of arrays will be observed for each BTEX compound to determine the most selective array. Using a single polymer-plasticizer pair to create multiple sensor coatings each with unique sensitivity and selectivity is of interest. Creating such a sensor array can reduce material costs and increase coating consistency. Sensitivity and selectivity of a sensor array created from polymer-plasticizer blend coatings with a single polymer-plasticizer pair will be analyzed to determine feasibility. The inclusion of coatings made from commercially available polymers can simplify coating composition in sensor arrays. The effects on sensitivity and selectivity of a sensor array containing coatings made from commercially available polymers as some members in the array will be analyzed.

1.7 Thesis Organization

This thesis is organized into five chapters. Chapter one offers an introduction to this research work. Rational for the work was presented and the problem statement was defined. An introduction to chemical sensing and sensors was presented, narrowing focus to polymer coated SH-SAW devices used as chemical sensors. Basic polymer properties and sensor arrays and associated necessary signal processing were discussed briefly. The focus of the work was narrowed to the analysis of arrays of polymer and polymer-plasticizer blend coated SH-SAW devices used for BTEX detection.

Chapter two offers detailed discussions of relevant theories and design aspects needed for the work. Design considerations of the SH-SAW device used in this work are discussed. Perturbation theory, polymer free-volume theory, and several plasticizer theories needed to understand the working principals of this work are discussed. Considerations made when designing polymer-plasticizer blends are presented, including solubility parameters, the effects of adding plasticizer on sensing parameters, and relevant polymer and plasticizer properties. Information on the formation of sensor arrays and principal component analysis necessary for selectivity analysis is presented. Finally, the polymers and plasticizers used for this work are presented and the arrays to be analyzed are formed.

Chapter three presents the equipment, materials, and procedures used in this work. Lists of all chemical materials and equipment used are detailed here. Experimental procedures are presented, including device preparation, coating solution preparation, device cleaning, spin coating, and analyte solution preparation. Procedures for coating thickness characterization, response measurement, analyte concentration confirmation and data processing are presented.

Chapter four contains a detailed analysis of sensitivity and selectivity of the proposed sensor arrays and discussion of results. Coating thicknesses and sensitivities and response time constants for each BTEX analyte are tabulated. Selectivity is compared using prepared charts and PCA analysis for each array individually. Arrays are compared to each other in terms of sensitivity and selectivity, and each goal specified is discussed in detail. The role of response time constant and extraction of multiple sensing parameters is discussed.

Chapter five contains a summary and conclusion of the work done for this research. Future work will also be discussed here.

2 THEORETICAL DISCUSSION

2.1 Introduction

An SH-SAW delay line device is a two-port device which can be used as a sensor platform. General design consists of a piezoelectric crystal and interdigital transducers in a delay line configuration. The piezoelectric crystal used for this work has a cut and orientation suitable for sensing in liquid phase. The selected cut is a 36° rotated Y-cut X-propagating lithium tantalate ($LiTaO_3$) piezoelectric crystal. This cut supports shear horizontal particle displacement, making it suitable for liquid phase operation [33]. Interdigital transducers (IDTs) generate mechanical stress when an oscillatory electric field is applied. The acoustic wave generated from this mechanical stress can be controlled to generate specific harmonics of the fundamental device frequency [39]. The SH-SAW device used in this work has input and output interdigital transducers (IDTs). IDT periodicity P_{IDT} is the distance between positive IDT fingers. A schematic view of an SH-SAW device used as a sensor is shown in Figure 2.1.

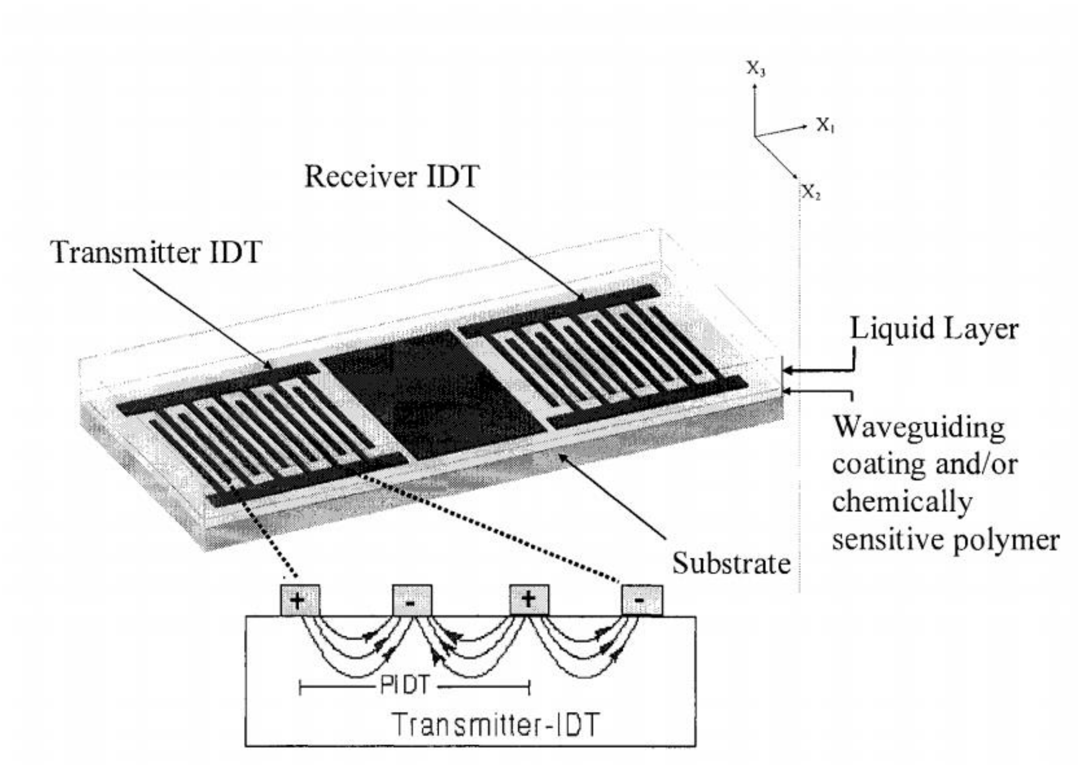

Figure 2. 1: Schematic view of two port SH-SAW device. Shown are transmitting and receiving IDTs, liquid layer, waveguiding/sensing layer, substrate layer, and IDT periodicity. [35].

SH-SAW particle displacement is in the horizontal direction (x_2 direction in Figure 2.1). As chemical sensors, acoustic wave devices are coated with chemically sensitive thin films for applications in gas or liquid phase [4, 8, 10, 12-16, 31, 34-38].

2.1.1 Sensor Geometry

Two geometries are associated with SH-SAW devices used for bio(chemical) sensing: 3-layer geometries and 4-layer geometries. This work utilizes a 3-layer geometry, which will be discussed further. This geometry consists of a substrate layer, a waveguide which also acts as a sensing layer, and a liquid layer. The waveguiding or sensing layer traps the acoustic energy near the device surface as well as provides sensitivity to target chemicals. Figure 2.2 shows a typical 3-layer sensor geometry.

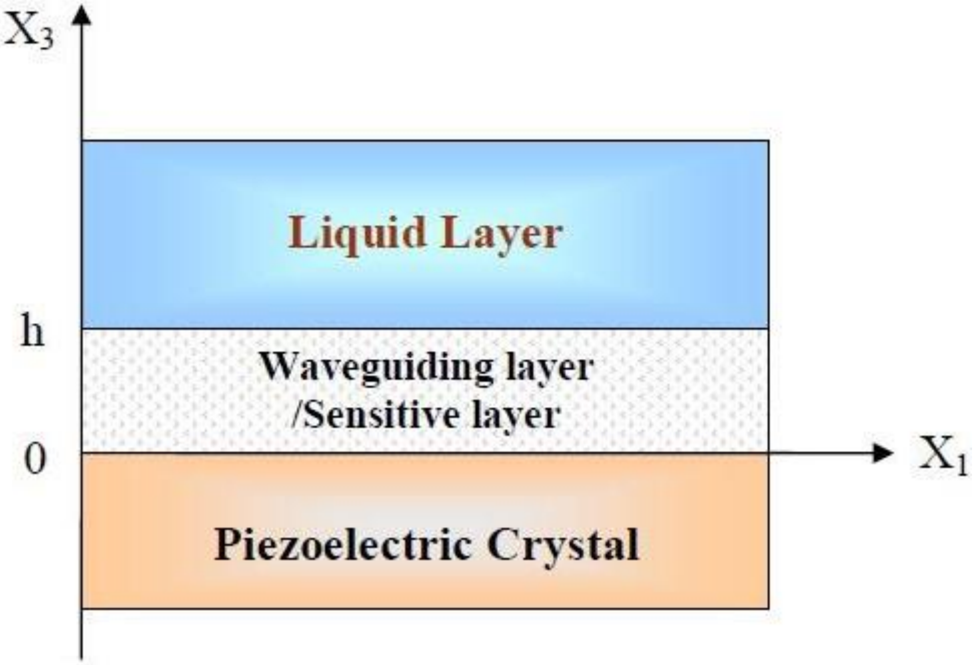

Figure 2. 2: Schematic view of 3-layer sensor geometry [37]

The waveguiding/sensing layers used consists of polymer or polymer-plasticizer blend sensor coatings. Several coated SH-SAW devices will be used to implement a sensor array. Coating composition will be presented in a later section.

2.1.2 IDT Configuration

IDTs are designed to achieve desired wavelength characteristics and to minimize acoustic reflections. IDT spacing dictates synchronous frequency, generating the fundamental acoustic mode and harmonics [32]. IDT finger pattern dictates which harmonics of the fundamental are generated. Figure 2.1 shows IDTs with a finger pattern of 1:1. A 1:1 pattern does not allow for the elimination of unwanted acoustic reflections or phase distortions. Reflection of the generated acoustic wave can occur at edges of IDT fingers which cause distortions in the transmitted wave, resulting in increased system noise [39]. A double IDT configuration (2:2 finger pattern) can eliminate much of the unwanted acoustic reflections. Paired fingers have opposite polarities, resulting in waves of the same amplitude with a 180° phase change. The amplitudes of the wave generated from the two opposite polarity fingers are assumed to be approximately equal, resulting in cancellation of the reflected waves [39]. The IDTs of the device used for this work have a 2:10 pattern designed to have a periodicity of 120μm. Measurements are performed using the third harmonic (λ = 40μm) which has a frequency of 103 MHz [39]. A diagram showing the IDT finger pattern and associated passband at the third harmonic of the SH-SAW device used in this work are shown in Figure 2.3.

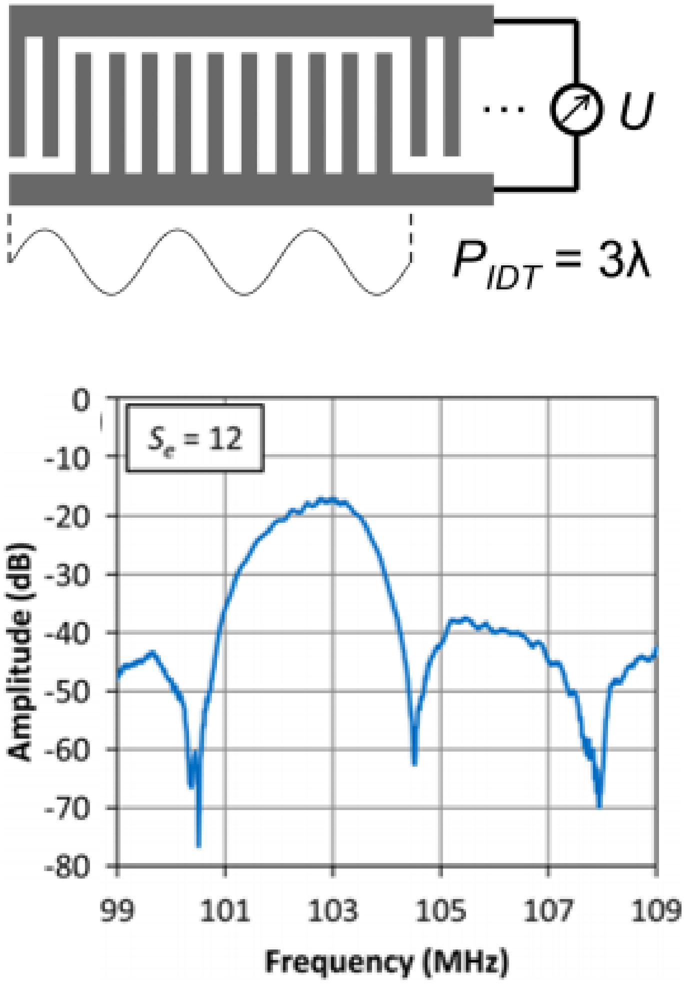

Figure 2. 3: Schematic view of 2:10 IDT finger pattern (top) with associated device passband frequency spectra of the sensing mode (bottom). S_e - number of electrode fingers per electrical period [39]

2.2 Sensing Mechanism and Perturbation Theory

The sensing mechanism of a coated SH-SAW device used as a chemical sensor is bulk absorption of target analytes. The sensor coating absorbs (and adsorbs) analyte, which, in turn, affects the acoustic wave velocity and attenuation [34, 35, 37]. Perturbation theory describes the interactions between coating and analyte. Small changes in wave velocity and attenuation can be written as a sum of partial derivatives as described in equations 2.1 and 2.2 [35].

$$\Delta V = \frac{\delta v}{\delta m}\Delta m + \frac{\delta v}{\delta c}\Delta c + \frac{\delta v}{\delta \varepsilon}\Delta \varepsilon + \frac{\delta v}{\delta \sigma}\Delta \sigma + \frac{\delta v}{\delta T}\Delta T + \frac{\delta v}{\delta P}\Delta P \qquad (2.1)$$

$$\Delta \alpha = \frac{\delta \alpha}{\delta c}\Delta c + \frac{\delta \alpha}{\delta \varepsilon}\Delta \varepsilon + \frac{\delta \alpha}{\delta \sigma}\Delta \sigma + \frac{\delta \alpha}{\delta T}\Delta T + \frac{\delta \alpha}{\delta P}\Delta P \qquad (2.2)$$

Changes in wave velocity (ΔV) can be attributed to changes in coating mass (m), viscoelastic constant (c), dielectric constant (ε), conductivity (σ), temperature (T) and pressure (P). Wave attenuation, ($\Delta\alpha$),depends only on viscoelastic and dielectric constants, conductivity, temperature, and pressure change [35]. By making several design considerations and taking appropriate steps during measurements, these equations can be further simplified. Using a dual delay line configuration and performing measurements in a temperature-controlled environment can eliminate temperature and pressure effects. A grounded metalized delay line can minimize changes in conductivity and dielectric constant by reducing acoustoelectric interactions. The resulting simplifications to equations 2.1 and 2.2 can be seen in equations 2.3 and 2.4 below [35].

$$\Delta V = \frac{\delta v}{\delta m}\Delta m + \frac{\delta v}{\delta c}\Delta c \tag{2.3}$$

$$\Delta\alpha = \frac{\delta\alpha}{\delta c}\Delta c \tag{2.4}$$

Analyte absorption causes changes in coating mass and viscoelastic constant, perturbing the wave velocity and attenuation. Perturbations in these parameters are measured as frequency shift and change in insertion loss. It is convenient to write the above equations in terms of the shear modulus (G). Because SH-SAW devices undergo shear deformation, only the shear modulus is of concern. Equation 2.5 breaks the shear modulus into real and complex terms, the shear storage (G') and shear loss (G'') moduli.

$$G = G' + jG'' \tag{2.5}$$

Equations 2.6 and 2.7 define change in wave velocity (or change in frequency) and attenuation in terms of the shear storage and loss moduli [35], with f_1 and f_2 representing functions of the given variables for simplicity.

$$\Delta f = f_1(\Delta m, \Delta G', \Delta G'') \tag{2.6}$$

$$\Delta\alpha = f_2(\Delta G', \Delta G'') \tag{2.7}$$

Measurement procedure dictates recording equilibrium frequency shift and insertion loss with a network analyzer. Insertion loss and acoustic wave attenuation are related by equation 2.8 [34]

$$\frac{\Delta\alpha}{k} = \frac{\Delta L}{54.6} N \tag{2.8}$$

where ΔL and N are change in insertion loss and length of the transmission line (units of wavelength, λ).

2.3 Polymer Viscoelasticity and Glass Transition Temperature

A polymer molecule consists of a long chain of repeated units called monomers. Monomers are formed from combinations of constituent atoms unique to each monomer [42]. Polymers fall into three general categories: thermoplastics, thermosets, and elastomers. Thermosets are polymers which undergo permanent deformation when heated or cooled. There is significant crosslinking between polymer molecules in thermosets. Thermoplastics are polymers which will return to their original structure when an applied stress is removed. There is significantly less crosslinking between polymer molecules in thermoplastics, which can be further separated into amorphous and crystalline thermoplastics. Elastomers are polymers which have properties between those of thermosets and thermoplastics. The polymer selected for this work is polystyrene, which is an amorphous thermoplastic [40, 42, 44].

2.3.1 Polymer Viscoelasticity

Viscoelasticity refers to a material property that indicates both viscous flow and elasticity. Viscous fluid flow is described by irreversible flow with a material having no defined shape of its own. Elasticity of a solid is a characteristic of a material to store energy and return to its original shape when stress is removed. Viscoelasticity refers to a material exhibiting properties of both a viscous liquid and an elastic solid. Depending on state, a viscoelastic material can store or dissipate energy as functions of temperature and time [40, 44].

2.3.2 Glass Transition Temperature

Glass transition temperature is one of the most important polymer properties [41]. Traditional transitions of matter (freezing and melting) are insufficient to describe the behavior of amorphous polymers. Amorphous polymers have glassy and rubbery regions depending on temperature. Between these regions is the transition region, where an amorphous polymer changes from glassy to rubbery [44].

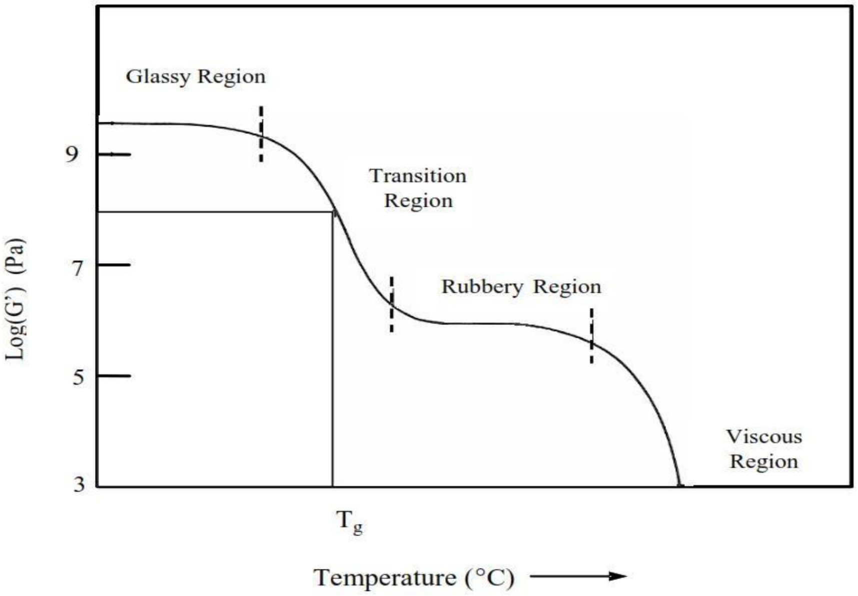

Figure 2. 4: Graphical representation of the glass transition temperature (log of the shear storage modulus vs temperature) [45]

Figure 2.4 shows all regions of an amorphous polymer from glassy to viscous. Between the glassy and rubbery regions is a region of transition where the glass transition temperature can be found. In this region, polymer properties such as stiffness, heat capacity, specific volume, and other viscoelastic properties change rapidly [40, 41]. T_g is typically defined as the midpoint of the transition region and is called the glass transition temperature. Free-Volume theory is useful in describing how the glass transition temperature arises.

Polymer free volume is the amount of space in a given volume which does not contain polymer molecules [40]. Total free volume of a polymer can be defined as the sum of the total free volume (V_f) and volume of polymer molecules (V_0) as given by equation 2.9 [40].

$$V = V_0 + V_f \tag{2.9}$$

Incorporating T_g, free volume can be further broken into fractional free volume. Fractional free volume will vary greatly inside of the transition region, beginning at the glass transition temperature. Below T_g, fractional free volume is defined as V_f^* and is effectively constant as shown in Figure 2.5.

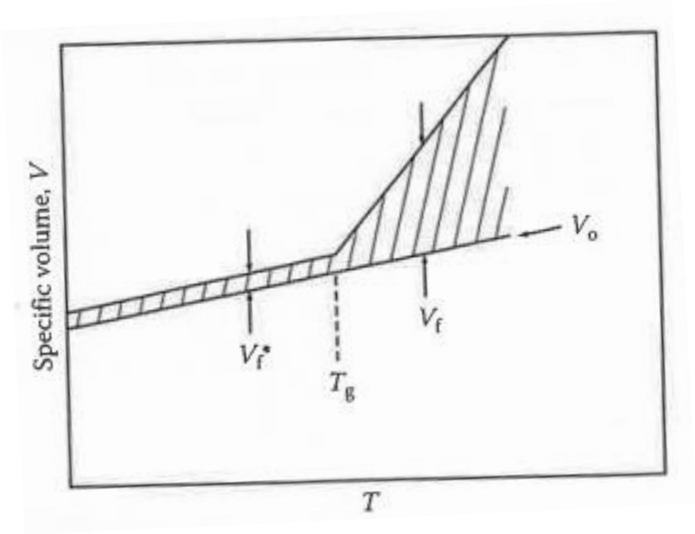

Figure 2. 5: Graphical representation of specific volume of a polymer versus temperature [40]

For temperatures above T_g, a new term V_f is defined. According to equation 2.10, the new free volume is equal to the previously constant free volume plus a derivative term related to both current temperature T and glass transition temperature T_g [40].

$$V_f = V_f^* + (T - Tg)\frac{\partial V}{\partial T} \tag{2.10}$$

Free volume is an important component in discussing plasticizer theories in addition to defining the glass transition temperature of a polymer. The next sections will take this concept and expand it by incorporating other properties to form a more complete view of free volume.

2.4 Plasticizer Theories

Plasticizers increase flexibility of previously rigid polymer molecules [46-48]. The primary application of plasticizers is to reduce a polymer's glass transition temperature [48]. The properties of each plasticizer are dictated by the polymer they are blended with, and as a result each polymer-plasticizer pair forms a unique blend with distinct properties. Therefore, it is difficult to identify fundamental properties common to all plasticizers [47]. There are two types of plasticizers, internal and external. Internal plasticizers are difficult to work with because they must be polymerized with the selected polymer. This work will use external plasticizers because only mixing of polymer and plasticizer in an appropriate solvent is required. There are several theories as to how plasticizers interact with polymer chains. Lubricity theory, Gel theory, and Free-Volume theory will be outlined in the following sections.

2.4.1 Lubricity Theory

Lubricity theory states that plasticizer decreases friction between individual polymer molecules. According to this theory, a polymer can be thought of as a stack of individual polymer molecules with free space between them. Plasticizer molecules enter the free space between molecules, reducing friction between them. Reduced friction increases overall flexibility of the polymer [48]. The result of blending plasticizer and polymer together according to Lubricity theory is to create alternating layers of polymer and plasticizer. An example of which can be seen in Figure 1.5.

2.4.2 Gel Theory

Gel theory is very similar to Lubricity theory. The primary function of plasticizer is to separate polymer molecules from one another. Gel theory describes a polymer as a three-dimensional honeycomb-like structure. Polymer molecules in this structure are connected to one another via attachment points. Plasticizer molecules separate some attachments between polymer molecules, reducing the total number of polymer-polymer interactions. This results in increased polymer flexibility [48].

2.4.3 Free-Volume Theory

Free-Volume theory states that the addition of a plasticizer to a polymer causes an increase in total free volume of the blend. Total polymer volume is described as the volume of polymer molecules plus the empty space (free volume) between polymer molecules. As shown in Figure 2.5 and indicated by equation 2.10, free volume will increase as temperature increases to T_g. At T_g there is a dramatic increase in free volume.

Rearranging equation 2.9 gives the total free volume as the difference between volume at the desired temperature and the volume at absolute zero. This is described by equation 2.11 as [48]:

$$V_f = V_T - V_0 \tag{2.11}$$

When plasticizer and polymer are mixed, plasticizer molecules insert themselves between polymer molecules and increase total free volume. Increased free volume also results in the lowering of the polymer's glass transition temperature [48].

2.4.4 Effects of Plasticizer on Sensing Parameters

In chemical sensing applications, it is important to determine how plasticization will affect sensing parameters. All described plasticizer theories indicate increased polymer flexibility. If a polymer is extremely rigid, sorption capacity will be low. Low sorption capacity can be directly linked to low polymer free volume. Increasing free volume will increase polymer flexibility, thus increasing the sorption capacity of the coating. Total sorption capacity is the natural sorption capacity of the polymer plus the added sorption capacity provided by the plasticizer [63].

Increased polymer flexibility, however, comes at the cost of higher device insertion loss when coated onto some devices. Flexible (rubbery) polymers typically result in increased acoustic wave attenuation as compared to glassy polymers. Increased wave attenuation is directly related to device insertion loss as indicated by equation 2.8.

The timescales of both attenuation and sorption will also affect insertion loss in measurements. Wave attenuation occurs at the measurement frequency (about 100MHz for the device used in this work). Analyte sorption happens on the timescale of minutes. These two modes of operation of the polymer coating cause rubbery behavior on the timescale of sorption but glassy behavior at the measurement frequency [64]. The relationship between insertion loss and sensitivity highlights one dichotomy present in these sensor coatings. Ideal sensor coatings have low noise (low wave attenuation, often found in glassy polymers) and high sensitivity to target analytes (high analyte sorption capacity, often found in rubbery polymers). Tradeoffs must be made to balance these two parameters for real world sensor coatings.

2.5 Solubility Parameters

Solubility of coating components (for this work, polymer and plasticizer) plays a key role in creating stable and reproducible coatings. The general rule of ‘like dissolves like’ is typically a good starting place for solubility considerations. This indicates that the polymer, plasticizer, and solvent used should all have some degree of molecular similarity. This similarity will ensure proper mixing of coating components as well as giving an indication of compatibility between coating and analyte. Miscibility between coating components can be observed using Hildebrand or Hansen solubility parameters [49]. Calculation of the Hildebrand solubility parameter (δ) can be performed using equation 2.12 which can be used to indicate miscibility of two materials [49].

$$\delta = \sqrt{c} = \sqrt{\frac{\Delta H - RT}{V_m}} \tag{2.12}$$

The above equation describes the Hildebrand solubility parameter (δ**)** as the square root of the cohesive energy density c, with heat of vaporization ΔH, ideal gas constant R, temperature T, and molar volume V_m.

Hansen solubility parameters are a more descriptive method of determining solubility. The Hansen solubility parameters break the Hildebrand parameter into three components. The dispersion forces (δ_d), dipole forces (δ_p), and hydrogen bonding (δ_h) relate to the Hildebrand solubility parameter by equation 2.12 [49-51].

$${\delta_t}^2 = {\delta_d}^2 + {\delta_p}^2 + {\delta_h}^2 \tag{2.12}$$

Hansen parameters can be used to compare miscibility of two materials more completely than the Hildebrand parameter can. A radius of interaction of two molecules is calculated using the Hansen parameters of each molecule.

$$(R_a)^2 = 4\left({\delta_{d2}}^2 - {\delta_{d1}}^2\right) + \left({\delta_{p2}}^2 - {\delta_{p1}}^2\right) + \left({\delta_{h2}}^2 - {\delta_{h1}}^2\right) \tag{2.13}$$

This radius of interaction R_a is compared to an experimentally determined radius of solubility (spherical region with radius $R_0 = 8.6$) to describe miscibility of solute and solvent. The Relative energy difference (RED) is then used to indicate miscibility of two compounds and is given by [51].

$$RED = \frac{R_a}{R_0} \tag{2.14}$$

A RED value greater than one indicates low/no miscibility between solute and solvent. A value below one indicates increasingly high miscibility with decreasing RED. Values of RED close to one indicate borderline cases where solute and solvent may or may not be miscible [51].

2.6 Selection of Coating Components

Proper component (polymer and plasticizer) selection is key to developing suitable sensor coatings for use in chemical sensing. Several desirable properties of polymers and plasticizers will be discussed in the next sections.

2.6.1 Polymer Properties

The ideal polymer for this work should have high sorption capacity and high selectivity for target analytes. High sorption capacity leads to high sensitivity and is characteristic of a rubbery polymer. Designing a coating with high analyte permeability and a fast and reversible response requires a polymer with low density and crystallinity. This indicates that a rubbery polymer is best for high sensitivity [53]. However, high selectivity is a characteristic of glassy polymers. A polymer should be selected such that the glass transition temperature indicates that it is either already rubbery or can be made rubbery with the addition of a plasticizer.

2.6.2 Plasticizer Compatibility

Plasticizer compatibility with the selected polymer is critical in sensor coating development. Factors effecting compatibility are polarity, molecular weight, and molecular shape of polymer and plasticizer [47]. Polarity of polymer and plasticizer relative to polarity of target analyte should also be considered. Non-polar coatings tend to favor absorption of non-polar target analytes and vice versa. RED values can be used to directly compare miscibility of polymer, plasticizer, solvent, and target analytes. RED values calculated for each group of polymer/plasticizer/solvent/analyte can indicate potential coating compositions even before work has begun. RED values can also indicate plasticizer leaching if insufficient miscibility is observed.

2.6.3 Plasticizer Efficiency

Efficiency describes how good a plasticizer is at plasticizing a given polymer. This is typically defined for the polymer it is paired with, as plasticizer properties vary for individual polymers. A plasticizer which reduces the glass transition temperature of a polymer to the rubbery region with a small volume of plasticizer is said to be efficient for that polymer [47]. Properties effecting efficiency include molecular mass, shape, and rate of diffusion of the plasticizer into the polymer. The faster the diffusion rate the higher the efficiency of the plasticizer. Fast diffusion rates lead to high plasticizer volatility, indicating the plasticizer will leach from the polymer more quickly. Volatility is typically a function of molecular size. Smaller plasticizer molecules will diffuse more quickly into the polymer but are more volatile in the coating [47].

2.6.4 Plasticizer Permanence

Permanence is a measure of how stable the plasticizer is in the polymer-plasticizer blend. Permanence of a plasticizer is dictated by rate of diffusion and molecular size of the plasticizer [47]. Plasticizer diffusion rate in a given polymer also affects its efficiency for that polymer. Plasticizer leaching is the phenomenon of a plasticizer leaving a polymer over time. Leaching indicates that permanence and efficiency are in direct conflict with one another. Smaller plasticizer molecules with fast diffusion rates lead to highly efficient plasticizers but also low permanence. Compatibility also has the potential to conflict with efficiency and permanence. The most efficient or permanent plasticizers may not be compatible with other coating components. Figure 2.6 represents the conflicting nature of the three properties of plasticizers discussed [47].

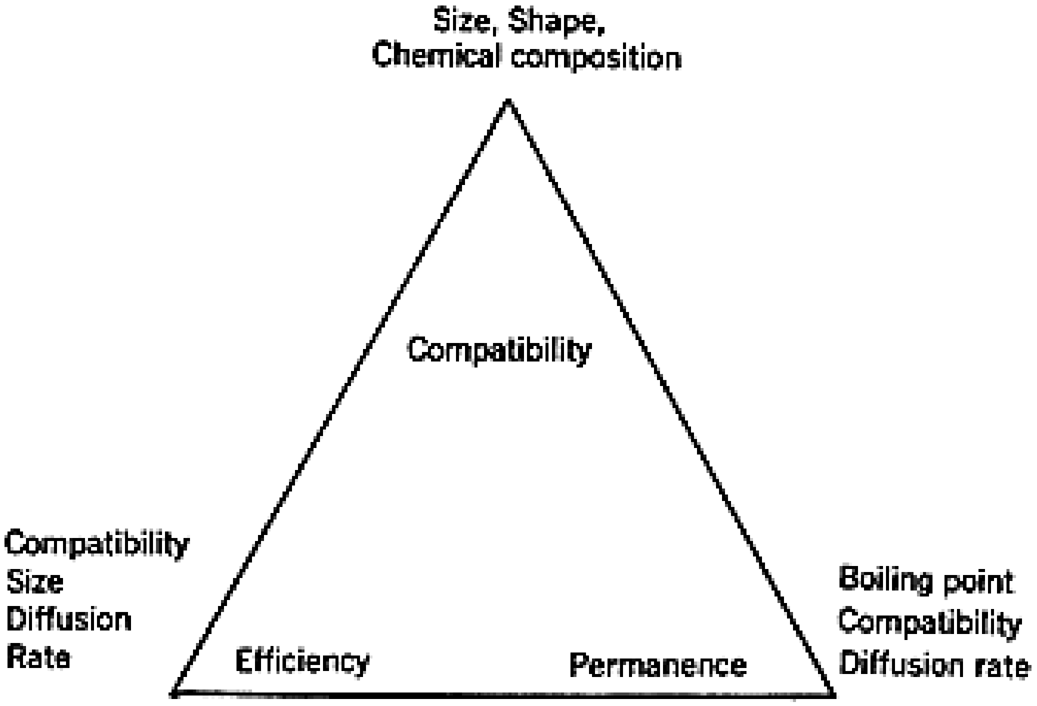

Figure 2. 6: Diagram showing the three properties of plasticizers discussed and the associated material properties which help in analysis of polymer-plasticizer affinity [47].

Coating thickness must also be considered when using a polymer-plasticizer blend as a sensor coating on various devices including acoustic wave devices. Coatings used for liquid phase measurements must use plasticizers which are relatively insoluble in water. Using highly efficient plasticizers in thick coatings leaves significant potential for leaching. Less efficient plasticizers with higher permanence allow for thicker sensor coatings.

2.7 Polymer-Plasticizer Blend Coatings for Sensor Arrays

Sensor arrays are used to increase selectivity beyond what a single sensor can achieve. The goal of a sensor array is identification and quantification of the target analyte, typically in single analyte solutions. Arrays work well for this task as each sensor coating can be designed to have a unique selectivity fingerprint. Initial work on polymer-plasticizer blend sensor coatings designed by our research group shows significant sensitivity to BTEX compounds [25, 37]. Sensor arrays using polymer-plasticizer blend sensor coatings would benefit from this high sensitivity to BTEX. Sensor arrays composed entirely of polymer-plasticizer blend coatings can be realized in one of two ways. Sensor coatings composed of different plasticizers and polymers can be developed. Sensor coatings composed of the same polymer-plasticizer blend in varied mixing ratios can be created. Both arrays have potential for high selectivity and high sensitivity to BTEX compounds.

2.8 Principal Component Analysis

One method of analyzing selectivity of a sensor array is performing principal component analysis (PCA) on data sets formed from the sensing parameters of each coating in the array. PCA uses the eigenvectors and eigenvalues of the correlation or covariance matrix of the formed data set to reduce dimensionality of the data [25]. If the majority of variance in the data set is captured in the first several principal components, those components can be used to represent the original data. Typically, 80-90% of the total variance is needed within the first one to two principal components to draw this conclusion [25]. If this condition is met, the principal components can be plotted to create clusters of data points. For this work, clusters represent the analytes which a sensor array is partially selective to. If analyte clusters are sufficiently separated from one another such that no points from clusters are overlapping, the array can be considered selective to those analytes. Increased separation between analyte clusters indicates higher selectivity with respect to those analytes. PCA combined with other indicators of selectivity will be used to characterize selectivity of the proposed sensor arrays.

2.9 Polymer and Plasticizer Selection

This work will focus on three different sensor arrays. For all polymer-plasticizer blend sensor coatings, the polymer polystyrene (PS) has been selected. The molecular structure of PS incorporates a benzene ring, which is beneficial for the detection of BTEX compounds [65]. The molecular structure of polystyrene can be seen in Figure 2.7.

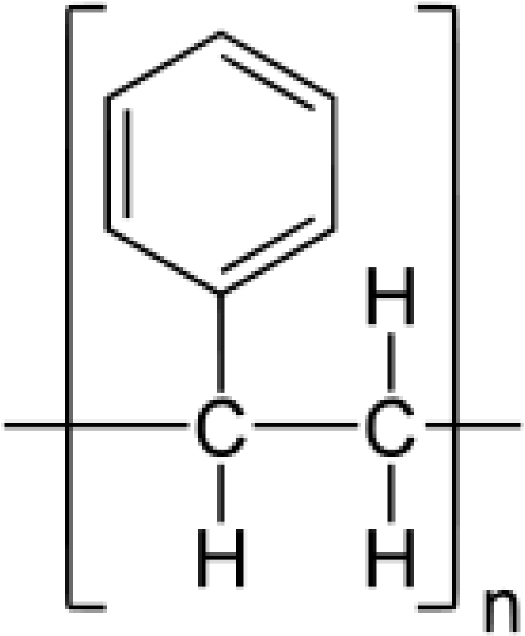

Figure 2. 7: Molecular structure of polystyrene [37]

PS has also been found to show high sensitivity to BTEX compounds when mixed with a plasticizer [37, 54]. The glass transition temperature of PS is 100-105°C [47]. A plasticizer can be added to lower the glass transition temperature, making PS suitable for this application.

The plasticizers used in this work are diisooctyl azelate (DIOA), 1,2-cyclohexane dicarboxylic acid diisononyl ester (DINCH), and ditridecyl phthalate (DTP). DIOA and DINCH plasticizers have both been used to develop sensor coatings by our research group [37, 54]. Molecular structures of DIOA and DINCH and a compiled table of solubility interactions with PS, solvents, and BTEX compounds can be seen in Figures 2.8 and 2.9 and Table 2.1.

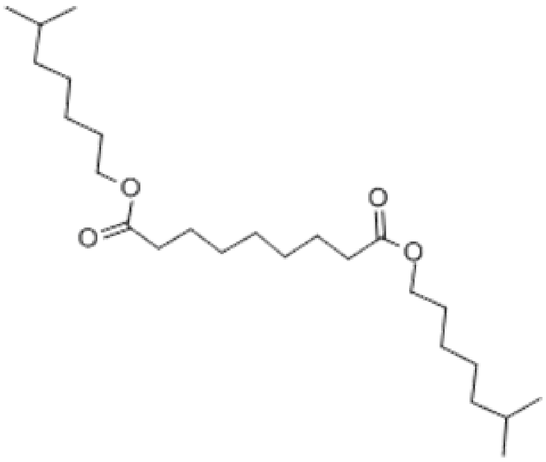

Figure 2. 8: Molecular structure of DIOA [37]

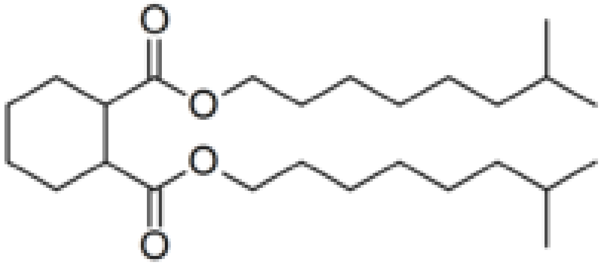

Figure 2. 9: Molecular Structure of DINCH [54]

Table 2.1: Summary of differential solubility parameters and RED for all relevant material compositions, adapted from [37]

First	Second	$\Delta\delta_d$	$\Delta\delta_p$	$\Delta\delta_h$	**RA**	**RED**
THF	DIOA	0.6	1	-0.4	1.612452	0.187494
THF	DINCH	1.4	-0.48	2.75	3.953846	0.45975
THF	Polystyrene	1.8	-1.2	-5.1	6.356886	0.739173
Benzene	Polystyrene	-0.2	-4.5	-0.9	4.606517	0.535642
Toluene	Polystyrene	-0.6	-3.1	-0.9	3.443835	0.400446
Ethylbenzene	Polystyrene	-0.8	-3.9	-1.5	4.474371	0.520276
xylene	Polystyrene	-1	-3.5	0.2	4.036087	0.469312
Benzene	DINCH	3	-6.18	-3.25	9.206242	1.070493
Toluene	DINCH	2.6	-4.78	-3.25	7.775018	0.904072
Ethylbenzene	DINCH	2.4	-5.58	-3.85	8.306558	0.965879
xylene	DINCH	2.2	-5.18	-2.15	7.128457	0.82889
Benzene	DIOA	-2.2	4.7	6.4	9.077995	1.055581
Toluene	DIOA	-1.8	3.3	6.4	8.050466	0.936101
Ethylbenzene	DIOA	-1.6	4.1	7	8.720665	1.014031
xylene	DIOA	-1.4	3.7	5.3	7.044147	0.819087
DINCH	PS	-3.2	1.68	2.35	7.021745	0.816482
DIOA	PS	-2.4	0.2	5.5	7.302739	0.849156

RED values represent the affinity of the pair of materials to each other. In Table 2.1, Green color indicates high affinity and yellow color indicates borderline cases where other factors may affect affinity. DIOA and DINCH have high affinity with PS, as indicated in Table 2.1. The borderline cases of DIOA and DINCH to benzene, toluene, and ethylbenzene are not an issue. The RED value of the blend will be a combination of the RED values of the coating components. Therefore, as each blend is majority PS the RED value of PS will dominate, indicating high affinity for BTEX compounds.

The final plasticizer selected for this work is DTP. There are no Hansen solubility parameters available for DTP. Blends of dioctyl phthalate (DOP) and PS have shown high sensitivity to BTEX compounds [54]. DTP and DOP are both phthalate-based plasticizers; as a result, properties similar to those of DOP are expected for DTP. Sensor coatings using DOP as plasticizer suffered from leaching due to DOP’s small molecular size (molecular weight 390.56 grams per mol, g/mol [55]). Coatings using this plasticizer were found to have a leaching rate of 0.8% per week [56]. DTP has a significantly larger molecular weight of 530.82 g/mol [55]. This increased molecular weight is expected to decrease leaching rate while maintaining high sensitivity. Figure 2.10 shows the molecular structure of DTP.

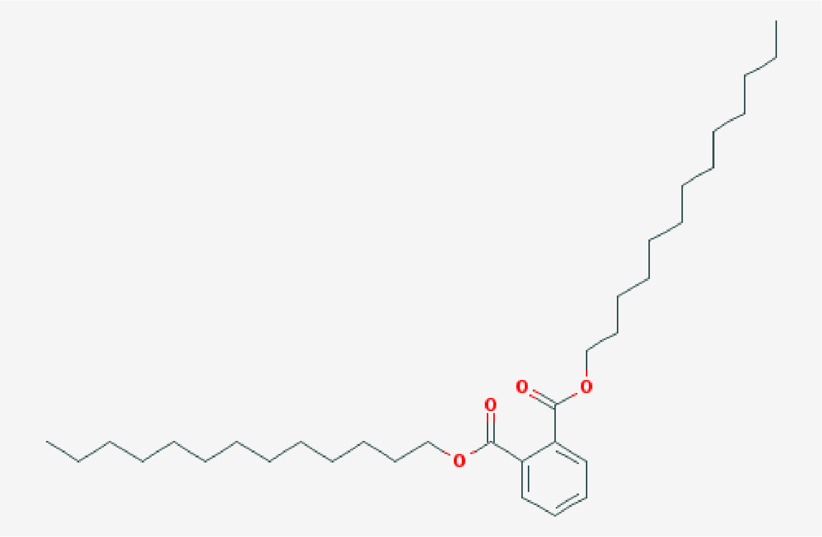

Figure 2. 10: Molecular structure of DTP [57]

Three sensor arrays are to be created using the above plasticizers in polymer-plasticizer blend sensor coatings. Two of the arrays proposed will consist entirely of polymer-plasticizer blend sensor coatings. One such array will utilize coatings with several unique plasticizers. The other will utilize coatings composed of a single polymer-plasticizer pair with a variable mixing ratio.

The third sensor array will consist of both polymer-plasticizer blend coatings and commercially available polymer coatings. The objective in using this array is to determine if including commercially available polymer sensor coatings in an array with polymer-plasticizer blend sensor coatings yields higher (partial) selectivity. The polymers poly(epichlorohydrin) (PECH) and polyisobutylene (PIB) have been selected for this array based on previous work with the coatings [66]. Molecular structures of PECH and PIB are shown in figures 2.11 and 2.12 respectively.

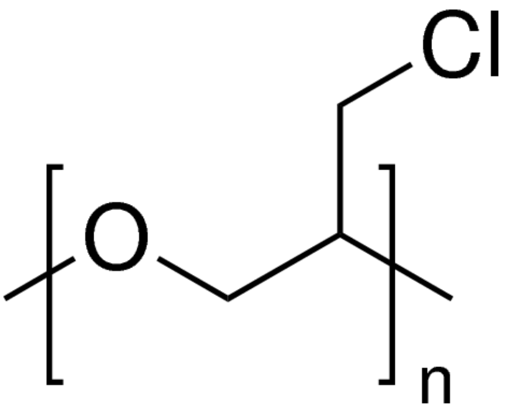

Figure 2. 11: Molecular structure of PECH [58]

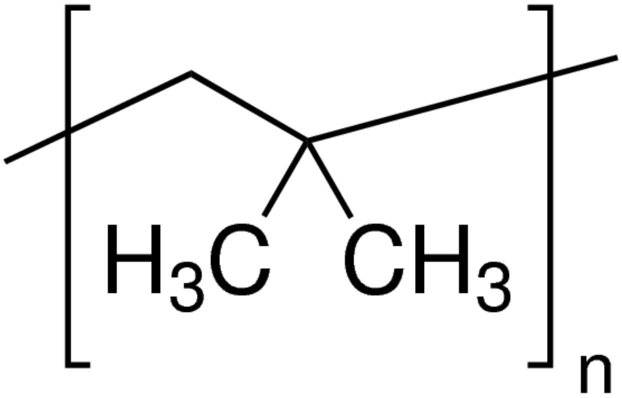

Figure 2. 12: Molecular structure of PIB [59]

3 MATERIALS AND PROCEDURES

3.1 Introduction to Materials and Procedures

This chapter details the materials, equipment, and procedures used in this work. Experimental procedures are as follows. Coating solutions are prepared by mixing designed blends of polymer and plasticizer in an appropriately selected solvent. Devices are cleaned using a four-step cleaning procedure to remove surface deposits/contaminants. Immediately after cleaning, devices are coated with a thin film of the blend using a spin coater. The coated devices are then baked to relax the thin film and remove any remaining solvent. A glass slide prepared alongside the sensor device is used for coating thickness characterization using a surface profilometer. Analyte stock solutions are prepared and diluted for use in measurements. The sensor device is placed inside of a flow cell and the cell is connected to a network analyzer. Measurements are recorded with an Agilent VEE computer program and sample concentration is quantified using a Gas Chromatography-Photoionization Detector (GC-PID). Details of each step outlined, materials, and equipment used are provided in the following sections.

3.2 Equipment and Materials

3.2.1 Chemical Materials

Several devices were selected to implement an array. Devices in the sensor arrays used for this work are all coated with polymer or polymer-plasticizer blend coatings. The polymer-plasticizer blends are designed using three commercially available plasticizers. 1,2-cyclohexane dicarboxylic acid Diisononyl ester (DINCH) [54] was obtained from BASF Corporation. Diisooctyl azelate (DIOA) [37] and ditridecyl phthalate (DTP) were purchased from Scientific Polymer Products. The polymer used for all polymer-plasticizer blends is polystyrene (PS) which was purchased from Sigma Aldrich. Polymer sensor coatings were made using commercially available polymers poly(epichlorohydrin) (PECH) and polyisobutylene (PIB) [35, 60], purchased from Sigma Aldrich. Coatings used either chloroform or tetrahydrofuran (THF) as solvent, which were purchased from Sigma Aldrich.

The chemical analytes used in this work are BTEX compounds purchased individually from Sigma Aldrich. Each compound has greater than 98% purity. Sample solutions of BTEX compounds were prepared using degassed DI water prepared at Marquette University.

3.2.2 Sensor Device

The device used in this work is an SH-SAW device designed at the Microsensors Research Lab at Marquette University [68]. Device substrate was selected as lithium tantalate ($LiTaO_3$). Deposited on the substrate are input and output gold IDTs and a gold metalized delay line (h = 70 nm), each with an adhesion layer of either titanium or chromium (h = 20 nm) underneath [68]. Delay lines are grounded to prevent electrical interaction between transducers in liquid phase measurements. The device operating frequency is 103MHz. Specific measurement frequency for a newly coated device is selected around this frequency and within the 3dB passband of the device to ensure phase linearity. A sensor device is shown in Figure 3.1.

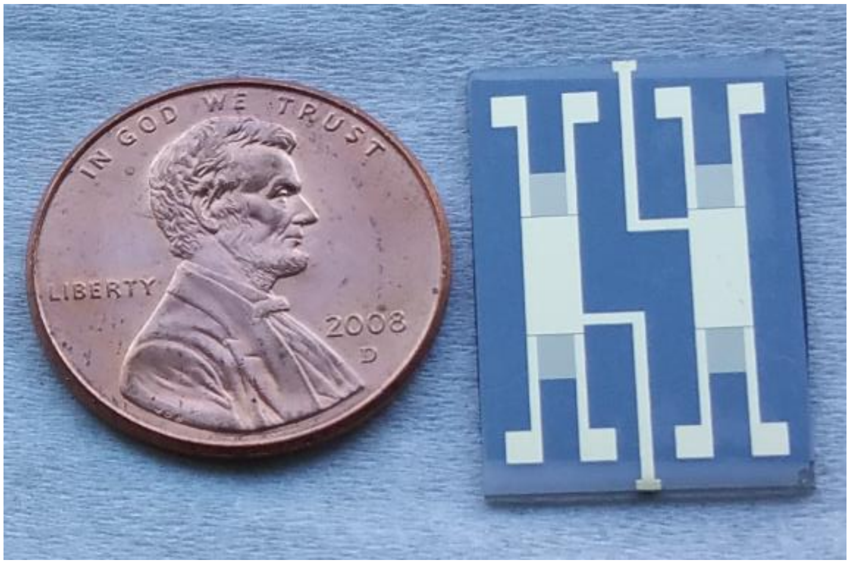

Figure 3. 1: Uncoated SH-SAW device shown next to a penny for scale.

3.2.3 Flow Cell

A coated SH-SAW device is housed in a specially designed flow cell during measurements. The three-part flow cell was designed for flow measurements for the Microsensors Research Lab [61]. The flow cell bottom is a brass base with a recess where the device is housed during measurements. The flow cell middle is a second brass component which acts to securely hold the device in place and to provide electrical connections with the device. This section has ten pogo pins which connect to each contact pad on a device. Input and output pogo pins connect to input and output ports which are, in turn, connected to a network analyzer for measurements. Ground pins are connected to the brass device housing to provide grounding for delay lines. The flow cell top is a piece of machined plexiglass which fits securely into the cavity in the flow cell middle. An air and water-tight seal is created by the gasket placed in a small groove contacting the sensor device. The cell bottom and middle and cell middle and top are connected each with four screws. Figure 3.2 shows each individual cell component.

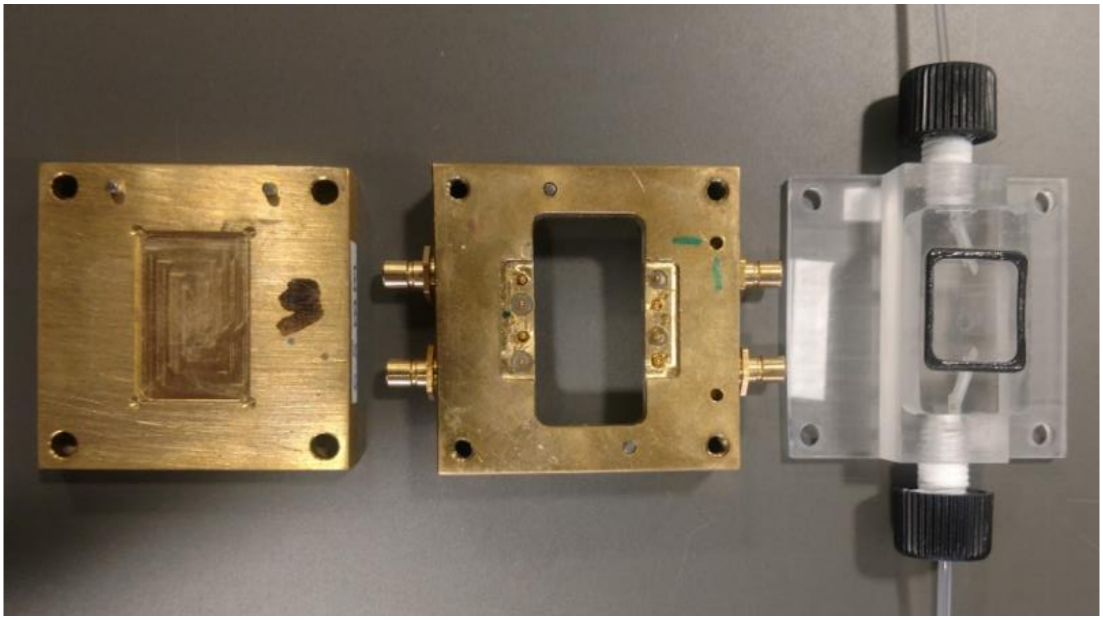

Figure 3. 2: Flow cell bottom (left), middle with pogo pins (center), and top with gasket (right) [69]

3.2.4 Spin Coater

Devices are coated using a Specialty Coating Systems (SCS) Model P6024 spin coater. Spin coater revolutions per minute (RMPs), ramp up and down time and speed, and total spin time can be controlled via “recipes” to achieve precise and reproducible coating thicknesses. Before spin coating, solution viscosity, solvent boiling point, and other characteristics must be considered. Precisely controlling the above parameters leads to repeatable and reproducible sensor coatings. A detailed description of coating deposition can be found in section 3.3.4.

3.2.5 Profilometer

Characterization of coating thickness is performed using a KLA-Tencor Alpha Step IQ Profilometer. This measurement method uses a moving sample table to drag a thin film underneath a stylus contacting the surface. A profile of the surface scanned is produced for each measurement performed. Scan length for this profilometer is fixed at 10 millimeters. Glass slides are prepared alongside devices when spin coating, as performing this mechanical measurement on a coated device could result in damage to the device. Kapton tape is used to create a gap of 6-8 millimeters on the surface of a glass slide. Taping in this manner allows for a differential step height measurement to be performed. A detailed description of steps for thickness characterization using a surface profilometer is provided in section 3.4.1.

3.2.6 Peristaltic Pump

Constant flow rate through the cell during measurements is provided by an Ismatec RS232 peristaltic pump manufactured by IDEX Corporation. The user can set flow rate, and for this work, a rate of 7µL per second was chosen. Samples are connected to the flow cell via a three-way valve and tubing. A diagram of the flow system will be discussed in section 3.2.8 and measurement procedure for recording sensor responses is discussed in section 3.4.2.

3.2.7 Network Analyzer

A vector network analyzer (Agilent E5061B) is used in this work to send input signals to the device and collect output signals. The network analyzer is connected to a switch control unit (Agilent 34980A) which switches between the two delay lines of the device. Device insertion loss, frequency, and phase data for each delay line are recorded as a function of time as the analyte sorbs into the coating using a program written in Agilent VEE visual programming language. Data is recorded at the chosen interval of 12 seconds. Initial frequency of measurement is selected for each new device as described in section 3.2.2 and is held constant for each successive measurement.

3.2.8 Gas Chromatography-Photoionization Detector (GC-PID)

After sensor responses are collected, concentrations of BTEX compounds are confirmed using a Defiant FROG 4000 Gas Chromatography-Photoionization Detector (GC-PID). The GC-PID uses a micro-preconcentrator, micro gas chromatography column, and micro photoionization detector to measure VOCs in water [62]. GC-PID calibration for BTEX compounds ranges from 10ppb-2ppm. Concentrations above this range begin to show non-linearity in GC-PID calibration curves and cannot be measured. If samples of higher concentration must be measured, they are first diluted down to lower concentrations. The GC-PID has an associated error of less than 10% inside of the calibration range.

3.2.9 Experimental Setup

A diagram of the experimental setup used in this work is shown in Figure 3.3. Sample jars containing degassed DI water (reference) and the diluted analyte solution are connected to the input terminals of a three-way valve. The output terminal of the three-way valve is connected to the flow cell input. Flow cell output is connected to a peristaltic pump, flowing into a waste container. Control of reference and analyte solution is done by selecting the appropriate input to the three-way valve. Coaxial cables connect the I/O terminals of the flow cell to the network analyzer. The network analyzer connects to a control computer which records data for each delay line at the selected interval.

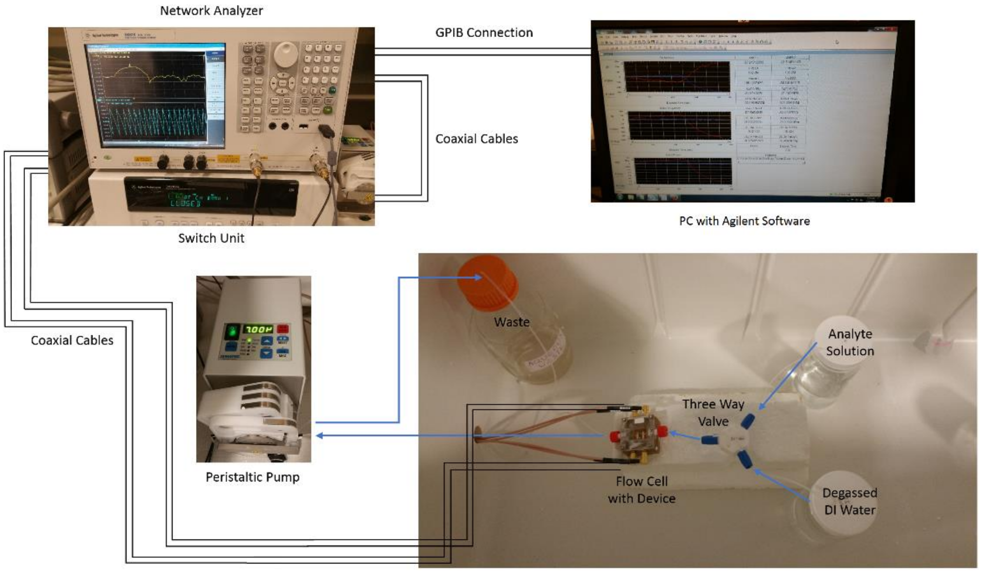

Figure 3. 3: Schematic view of experimental setup. Desired sample is selected via the three-way valve and flowed over the device. Responses are recorded via coaxial connections to network analyzer controlled by Agilent VEE program.

3.3 Preparation Procedures

3.3.1 Preparing a Device

New SH-SAW devices are prepared appropriately before they can be used for measurements. These preparation steps ensure that new devices perform optimally. The goal of preparation is to reduce passband ripple and unwanted acoustic reflections. Preparation steps are as follows.

1. Record the passband of a new unfiled device with a network analyzer for later comparison with finished device.

2. Use course grit sand paper (#40) to file short sides of device to approximately a 45° angle. Caution should be used during this step as devices are extremely fragile.
3. Use same sandpaper to file a groove between each set of contact pads on the short side of the device to scatter prevent any reflected acoustic wave to reach the IDT.
4. Observe the passband of the newly filed device and compare to the original passband. Passband ripple should be significantly reduced, resulting in smooth acoustic modes.

Before any proceeding steps/procedures are followed, the passband of a device should always be recorded for future comparison to ensure proper operation.

3.3.2 Coating Solution Preparation

Coating solutions using commercially available polymers use a weight ratio of polymer to solvent. With the addition of a plasticizer, two weight ratios are used. A weight ratio of plasticizer to polymer is first determined, and then a weight ratio of total polymer and plasticizer to solvent is used to complete the blend. Varying plasticizer percentage of a polymer-plasticizer blend can produce differences in coating performance during measurement (sensitivity, selectivity, etc.). Varying the amount of solvent used will affect coating thickness from spin-coating. Polymer-plasticizer blend coating solutions are prepared according to the following procedure, in which equations 3.1 and 3.2 are used.

$$wt\% = \frac{mass\ of\ plasticizer\ (g)}{total\ mass\ of\ plasticizer\ and\ polymer\ (g)} x100. \tag{3.1}$$

$$wt\% = \frac{mass\ of\ polymer\ and\ plasticizer\ (g)}{total\ mass\ of\ solution\ (g)} x100. \tag{3.2}$$

It should be noted that for non-plasticized coating solutions, equation 3.2 is used directly. Steps used to prepare coating solutions are as follows.

1. Clean the vial which will be used with an appropriate solvent. This will ensure that no impurities make their way into the final blend.
    a. Fill desired vial halfway with the solvent being used in the blend and place a magnetic stir bar in the vial. Close lid tightly.
    b. Place on a magnetic stir plate and stir for 5 minutes.
    c. Flip vial upside down (lid should now be contacting stir plate). Stir 5 minutes.
    d. Flip vial right-side-up. Stir a final 5 minutes.
    e. Empty vial of solvent and allow to dry completely before proceeding.
2. Place the cleaned and dried vial with magnetic stir bar on a microbalance and zero the balance.
3. Add the desired mass of polymer to the vial. Without zeroing balance, calculate the necessary mass of plasticizer according to the blending ratio desired by using equation 3.1. NOTE: Performing calculation in this way will yield the total mass of polymer and plasticizer needed, not the individual mass of plasticizer. It is important to not zero the microbalance during any point in the process of preparing a coating solution after initial zeroing.

4. Add the calculated mass of plasticizer. Without zeroing balance, calculate the necessary mass of solvent to add using equation 3.2.
5. Add the calculated mass of solvent. Quickly close the lid and seal with Teflon tape to prevent solvent evaporation.
6. Place vial on magnetic stir plate and allow to stir overnight at ~600-700 rpm.
7. Remove vial from stir plate. Place vial in ultrasonic bath for 4 hours.
8. Remove from ultrasonic bath. Allow to cool to room temperature before using solution to coat sensor devices.

3.3.3 Device Cleaning Procedure

For reproducible coatings with good adhesion to device surfaces, proper device cleaning procedures must be followed. The following cleaning procedure removes any previous polymer coatings, residues, conductive silver paint, or other organic contaminants from the surface. Improper device cleaning can result in formation of pinholes or other imperfections which lead to non-reproducible coatings. The device cleaning procedure is as follows (NOTE: the same cleaning procedure should be used for glass slides as well).

1. Any tape on device surfaces should be removed. This includes Kapton tape on the device surface and black tape on the bottom of a device.
2. Devices should be placed in jars containing one of four successive solvents. Trichloroethylene, chloroform, acetone, and isopropanol are used as cleaning solvents. No more than one device should be placed in the same jar at a time. Jars are placed in a sonication bath which agitates the contents of the jars and damage

to devices could occur during this process with multiple devices in a jar. The following procedures should be observed for each solvent step.

  a. Place device in jar containing the appropriate solvent.
  b. Close the jar. Place in ultrasonic bath for 5 minutes.
  c. Remove jar from ultrasonic bath. Remove device from solvent and rinse with DI water for 30 seconds.
  d. Dry device with nitrogen gas.
  e. Repeat a-d for trichloroethylene, chloroform, and acetone steps. For isopropanol step, do not rinse with DI water and proceed directly to drying device with nitrogen gas.

3. Devices should be coated as soon as possible after cleaning to prevent re-deposition of contaminants on the device surfaces. Additional cleaning steps are provided in steps 4 and 5. Taping and coating should be performed as soon as the final cleaning step performed is completed.
4. Prepare a mixture of 5:5:1 $H_2O:NH_4OH:H_2O_2$. Heat solution to 65-70°C. Place device in heated solution for 5 minutes. Remove and rinse with DI water for 30 seconds.
5. Place device ~1 centimeter from a UV lamp. Allow device to sit beneath lamp for 1 hour.
6. Kapton tape should be placed to cover the contact pads of a device. When taping a glass slide, a 6-8mm gap should be left in between tape segments. This allows for thickness characterization as described in section 3.2.5. Excess tape should be

removed. Devices are now ready for coating, which should be performed as soon as possible.

3.3.4 Spin Coating, Baking, and Device Preparation Procedure

Following proper spin coating procedure ensures that reliable and reproducible coatings are deposited. Proper procedure for spin coating is as follows.

1. The spin coater is initialized when a source of air flow is detected. Open the lab air valve connected to the spin coater to initialize the machine. Plug in the vacuum pump to provide a source of vacuum to the spin coater.
2. Select appropriate spin coater settings. RPM rate, ramp up/down time, ramp up/down speed, and spin time can be controlled as described in section 3.2.4.
3. A cleaned and taped device is placed on the center of the vacuum chuck. Ensure that the device is properly centered. Failing to properly center the device will lead to uneven/non-reproducible coatings.
4. Using a micropipette, deposit 350µL of coating solution onto the center of the device. If the solution is very viscous, it should be distributed evenly across the device surface to ensure the entire device is coated.
5. Quickly close spin coater lid and press start button to begin spinning procedure.
6. After spin coating has finished, remove device and place in aluminum baking dish.
7. Repeat steps 3-6 for all devices to be coated. If more than one spin speed is needed, repeat steps 2-6 instead.

8. After coating all devices, place lid on aluminum baking disk. Place in oven and bake according to the needed temperature and time of coatings deposited. For coatings used in this work, baking is done at 60°C for 60 minutes.
9. Turn off oven. Allow devices to cool at least 30 minutes.
10. Remove dish from oven. Remove Kapton tape from individual devices. Devices are now ready to be prepared for measurements.
11. Black absorbing tape should be placed on the back of devices. This ensures devices sit properly in the flow cell bottom. Smooth tape on back of the devices to remove bubbles/particles underneath tape. Trim excess tape from the device edges using a scalpel.
12. Conductive silver paint is deposited onto device contact pads to ensure proper connection between the pads and the flow cell pogo pins. Avoid accidental connection of electrical contacts. Allow to dry for at least 15 minutes before putting the coated, taped, and silver painted device into a flow cell for measurement.

3.3.5 Analyte Solution Preparation

Consistent sample preparation is important for repeatable measurement results. To ensure consistent sample preparation at low concentration, stock solutions are prepared and diluted to the target concentrations. The procedures for preparing analyte samples are as follows:

1. Prepare needed amount of degassed DI water.
    a. Fill a large flask with DI water.
    b. Place flask without stopper on a hot plate. Set hot plate to 250-300°C.

    c. Allow water in flask to reach boiling point. Once boiling, allow DI water to boil an additional 2 hours.
    d. Turn hot plate off and allow flask to remain on hot plate for 30-40 minutes to cool.
    e. Remove flask from hot plate and place stopper in top of flask. Allow to cool to room temperature before use. DI water will now be degassed.

2. Select jar in which stock solution will be prepared. Fill selected jar to top with degassed DI water. Ensure that there is little head space left in jar before replacing lid.
3. Calculate the necessary volume of analyte chemical needed to produce a stock solution of desired concentration in the prepared volume of DI Water.
4. Remove calculated amount of analyte with micropipette and eject pipette tip containing analyte into DI water jar. Close lid tightly. This step must be performed quickly as analytes are volatile.
5. Place stock solution on a magnetic stir plate. Stir at ~700 rpm at least 4 hours. Stock solution is now ready for dilution.
6. Fill desired jars with degassed DI water as in step 2. These jars will be used to dilute stock solution to desired concentrations.
7. Calculate volume of DI water to remove based on desired diluted concentrations. Remove this calculated amount of DI water from each individual jar.
8. Remove stock solution from stir plate. Deposit calculated amount of analyte solution into each sample jar. Close lids to each jar tightly.

9. Place each jar of diluted analyte on magnetic stir plate. Stir at ~500 rpm for at least 1 hour. Samples are now ready to use.

3.4 Measurement Procedures

3.4.1 Coating Thickness Characterization

Thickness characterization is performed each time a new device is prepared for measurement. This is done to obtain initial thickness values for new coatings and to confirm thicknesses of devices. Measurements are performed on glass slides prepared alongside devices according to the procedures previously discussed. A surface profilometer is used to obtain a series of step height measurements, which yield the coating thickness. The measurement procedures for coating thickness characterization are as follows:

1. Surface profilometer is turned on. Stylus force is set to 0.2-0.5mg. This force is selected so as to not deform the soft polymer coating.
2. The glass slide to be measured is placed on the measurement table. The measurement table is raised until the stylus is in contact with the glass slide. Coating thickness is measured using a differential step height using uncoated glass slide on either side of the coated surface for baseline correction. Position the stylus to collect an appropriate scan of the coating surface.
3. Press start button to perform a scan.
4. After the scan is finished, the scan data is processed.

   a. Baseline correction is performed using the leveling feature. A third order correction is applied, with exclusion of the coating. This ensures a flat baseline.
   b. Filtering is performed to remove measurement noise using the filtering feature. 25µm filtering is typically selected to smooth the scan data.
   c. Step height measurement is selected to perform a differential step height measurement.

5. Coating thickness for the scan performed is indicated in angstroms (Å). Steps 3-5 are repeated several times until an average coating thickness can be obtained.

3.4.2 Coating Response

Newly coated devices are placed inside the flow cell to collect device responses to various analyte solutions. Consistent measurement procedures allow for minimization of external noise in the system, leading to more accurate results collected in a single measurement and more repeatable and reproducible results collected across measurements. The procedures for collecting a sensor coating response to an analyte solution are as follows:

1. Sample jars, DI water jar, and flow cell with device are placed in a temperature control chamber and connected to flow system (see Figure 3.3 for configuration).
2. The flow cell cavity is filled with the fluid under test and any residual air pockets are removed.
3. Passband spectrum of the device is recorded prior to sensor measurements for comparison with previous spectra.

4. An Agilent VEE program is used to monitor amplitude, frequency, and phase of the device under test.
5. Individual responses of coated sensor devices to chemical analytes contain three components: initial baseline, absorption response, and desorption return to baseline.
    a. Sufficient initial baseline is recorded. DI water is allowed to flow over the device and the sensor output is recorded. This allows for correction of linear baseline drift in data processing after measurements are completed.
    b. The three-way valve input is switched to sample. This step should be performed as quickly as possible to minimize time spent inside of the temperature control chamber. Coating absorption response is collected until frequency shift reaches an equilibrium or steady-state. This is dictated by the response time of the coating to the analyte under test.
    c. Once steady-state response has been reached, the three-way valve is returned to the DI water input. Sensor response returns from the previous state to the initial baseline. The desorption response time is approximately the same as the absorption response time.
6. Step 7a-c are repeated for each analyte sample being measured.

3.4.3 Analyte Concentration Confirmation

For measurements with BTEX compounds, concentration of analyte samples is confirmed using a GC-PID. Measurement procedure for confirming analyte concentration are as follows:

1. GC-PID is turned on and the measurement program is started.
2. A blank measurement (water blank) is run prior to sample measurement. Water blanks ensure that there are no lingering BTEX compounds in the GC-PID column by performing a measurement with only DI water instead of analyte solutions. The test tube is connected via clamp, and exactly 5mL of DI Water is transferred into the tube.
3. The valve input is closed, indicating the measurement is ready to start. Press start button, checking if bubbles can be seen in test tube to ensure proper operation. A full measurement takes approximately 10 minutes to complete.
4. After completion of a blank measurement (water blank), results should be checked to ensure no BTEX compounds were detected. If BTEX compounds are detected in the water blank, another blank measurement must be run. It may take several water blanks to remove all BTEX compounds from the column. When results indicate that no BTEX compounds remain in the column samples may be tested.
5. The test tube is replaced and clamped. Input valve is opened and exactly 5mL of analyte solution is inserted into the tube.
6. The input valve is closed, and a measurement is started.
7. After the measurement is completed, data is analyzed by the software. The program indicates each analyte identified in the sample and the measured concentrations.
8. Data is saved in the form of a PDF file of the measurement results.

These steps are repeated for every tested sample.

3.4.4 Data Processing

Measurement data is recorded by an Agilent VEE program as .CSV files. From these files, individual measurements must be extracted and appropriately processed. Individual measurement responses are separated and corrected for linear baseline drift before further processing can take place. An exponential curve fitting program can take baseline corrected absorption and desorption responses individually and extract parameters of interest. The curve fitting program used has been written in MatLab in the Microsensors Research Lab and extracts steady-state frequency shift and response time constant of a measurement. The average frequency shift for each BTEX analyte is calculated from each measurement response after being normalized to 1ppm analyte concentration by using equation 3.3

$$f_n = f_0 \left(\frac{C_n}{C_0}\right) \tag{3.3}$$

where f_n is normalized frequency shift, f_0 is extracted frequency shift, C_n is the normalization concentration (1 ppm analyte), and C_0 is the measured analyte concentration from the GC-PID. Sensitivity of each sensor coating to each BTEX analyte is in Hz/ppm, and is given by equation 3.4 as:

$$S = \frac{\Delta f}{C_0} \tag{3.4}$$

Additional data processing for the sensor array selectivity analysis is performed in the form of PCA. A MatLab program has been written in the Microsensors Research Lab which performs PCA using selected input parameters [25]. The input parameters used for the PCA analysis are the coating sensitivity and response time constant for each BTEX analyte. Parameters are formed into a data set, the correlation matrix of the data set is formed, and eigenvectors and eigenvalues are calculated. The indicated number of principal components are then computed and used for analysis of each array [25]. In this work, the first two principal components of the data set are plotted in order to visually represent selectivity of each array. Separation of individual clusters indicates how selective a given array of coatings is to each BTEX analyte.

4 RESULTS AND DISCUSSION

4.1 Introduction to Results

The focus of this research is to analyze sensor arrays comprised of polymer coatings and polymer-plasticizer blend coatings with emphasis on high sensitivity and high selectivity. Coatings used include those newly investigated for this work as well as those investigated by previous students in the Microsensors Research Lab. Sensor coatings are tested using single analyte solutions of BTEX compounds with concentrations ranging from 50 ppb to 1.5 ppm.

Measurements are conducted, and sensor signal data are processed according to the appropriate procedures presented in chapter 3. Exponential curve fitting is used to extract equilibrium frequency shift and response time constant from every individual sensor response measurement. Equilibrium frequency shifts are normalized to 1 ppm analyte concentration and averaged for each analyte to obtain average sensitivity (units of Hertz per ppm, Hz/ppm). Response time constants are averaged for each analyte to obtain average response time (units of seconds). Standard error is calculated for both average sensitivity and response time constant.

The calculated average sensitivities and time constants are used to create three plots for each array. Average sensitivities for toluene, ethylbenzene, and xylenes are normalized with respect to analyte solubility, analyte molar mass, and average sensitivity to benzene. First, normalized sensitivities are used to create bar charts which are good indicators of partial selectivity for a specific coating in a sensor array. These charts provide a selectivity fingerprint for the array formed from the coatings indicated. Next, selected time constants and ratios of sensitivities of each analyte for each coating in an array are displayed using a radial plot. Plotting in this fashion allows for visualization of separation of data for each coating and analyte and can be used as an indicator of selectivity. These plots also allow for the removal of some redundant information present in time constant or sensitivity data. When data from two separate time constants or sensitivity ratios are very similar, one can be selected to simplify the plot. Finally, average sensitivities and time constants of each BTEX analyte for each coating in an array are used as an input data set for principal component analysis (PCA). The reduced data set obtained from PCA is plotted as a two-dimensional graph featuring clusters attributed to each analyte tested. The separation between analyte clusters on this plot can be used as an indicator of selectivity of the array.

All plots for each array of different coatings will be presented and discussed in detail to describe the sensitivity and selectivity of each array. Next a comparison of sensitivity and selectivity of all arrays will be presented, and a discussion of important factors in identifying selectivity of each array.

4.2 Sensor Coatings and Array Definition

4.2.1 Previously Investigated Sensor Coatings

Four coatings used to create sensor arrays in this work have been previously investigated [37, 54, 66]. Coatings include 2.5% PIB and 4% PECH polymer coatings (dissolved in chloroform) [66] and 23% DINCH-PS (dissolved in THF) [54] and 17.5% DIOA-PS 11.5% in THF [37] polymer-plasticizer blend coatings. These specific DINCH-PS and DIOA-PS coatings were selected because they are both the final blends presented in [37] and [54] respectively. It was found that each of these two polymer-plasticizer blend coatings has high sensitivity to BTEX analytes. PIB and PECH are rubbery without the addition of plasticizer and show modest sensitivity to BTEX analytes. Tables 4.1 and 4.2 below summarize thickness and average sensitivity and response time for each BTEX analyte of the four coatings discussed.

Table 4.1: Summary of sensor coating thicknesses and sensitivities for each BTEX compound [37, 54, 66].

Sensor Coating	Thickness (μm)	Benzene Sensitivity (Hz/ppm)	Toluene Sensitivity (Hz/ppm)	Ethylbenzene Sensitivity (Hz/ppm)	Xylenes Sensitivity (Hz/ppm)
2.5% PIB in Chloroform	0.8	78 ± 7	403 ± 39	1160 ± 57	1160 ± 57
4% PECH in Chloroform	0.6	109 ± 9	435 ± 25	1450 ± 240	1450 ± 240
17.5% DIOA-PS 11.5% in THF	1.25	450 ± 50	1510 ± 200	3450 ± 500	7030 ± 700
23% DINCH-PS	1.0	240 ± 30	810 ± 50	2010 ± 500	2520 ± 250

Table 4.2: Summary of sensor coating response time constants for each BTEX compound [37, 54, 66].

Sensor Coating	Benzene Time Constant (seconds)	Toluene Time Constant (seconds)	Ethylbenzene Time Constant (seconds)	Xylenes Time Constant (seconds)
2.5% PIB in Chloroform	36 ± 7	88 ± 12	230 ± 12	230 ± 12
4% PECH in Chloroform	27 ± 8	78 ± 3	175 ± 13	175 ± 13
17.5% DIOA-PS 11.5% in THF	101 ± 10	238 ± 25	576 ± 50	648 ± 50
23% DINCH-PS	70 ± 7	140 ± 14	364 ± 50	358 ± 55

4.2.2 DTP-PS Sensor Coatings

Five sensor coatings have been investigated for this work which have not been previously characterized. These coatings utilize a single polymer-plasticizer pair as coating blend components with a variable blending ratio and have been designed to all have a uniform thickness. Plasticizer ditridecyl phthalate has been blended with polymer polystyrene at mixing ratios of 22%, 30%, 32%, 33.5%, and 35% weight percentage plasticizer to polymer.

DTP-PS blends were designed to ensure a uniform thickness across all coatings. 1.3µm-thick layer was selected for the final thickness, as coatings showed increasing sensitivity up to this thickness. Beyond this thickness, most coatings showed drastically reduced stability.

Measurements with each coating were performed over a number of weeks to months depending on coating stability. As plasticizer percentage is increased, coatings become increasingly prone to instability and degrade (i.e., form pinholes in the coating, leach plasticizer, etc.) at a faster rate. To ensure proper device function before every measurement, a frequency spectrum is recorded, and a consistent measurement frequency is selected. The selected measurement frequency is unique to each newly coated device, but all are selected within the 3dB passband of the device center frequency of 103MHz and near 0° phase to ensure linearity over a wide range of frequencies. Shown in figure 4.1 below is a sample passband frequency spectrum of a coated device.

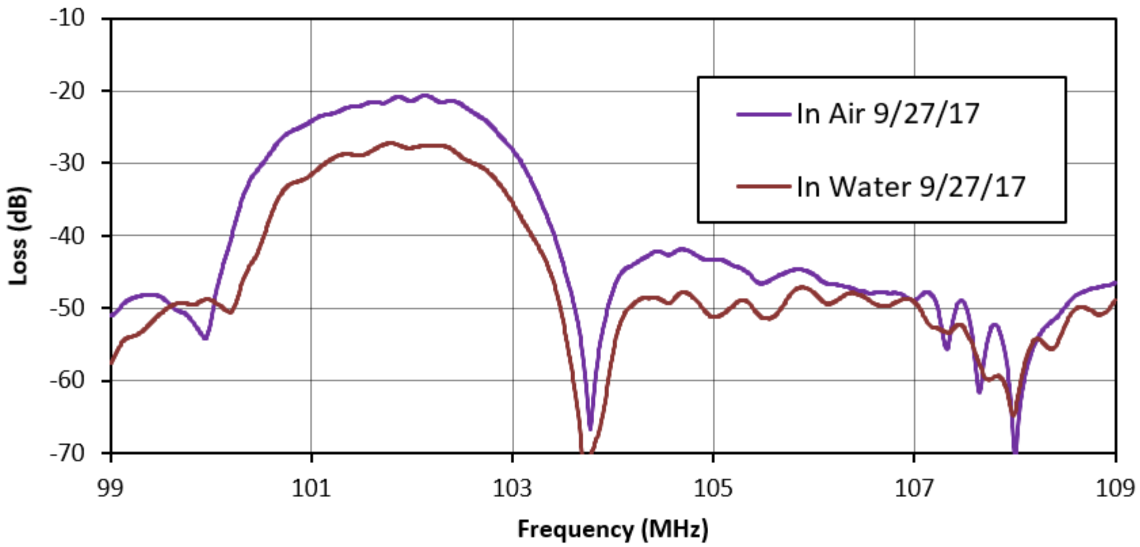

Figure 4. 1: Passband frequency spectrum indicating coating insertion loss of an SH-SAW device coated with a 30% DTP-PS 7% in chloroform coating. Shown are two curves: in purple is the frequency spectrum of the coated device in air before measurements are performed and in red is the frequency spectrum of the coated device in water just prior to a measurement. When measuring in liquids, the acoustic wave is attenuated more than in air, resulting in a higher (more negative) insertion loss for liquid phase measurements. An increase of 6-8dB is typical for a coated device.

Coating responses have been collected for various concentrations of single analyte solutions of BTEX compounds. A sample sensor response of a device coated with a 30% DTP-PS coating to 1 ppm benzene is shown in figure 4.2.

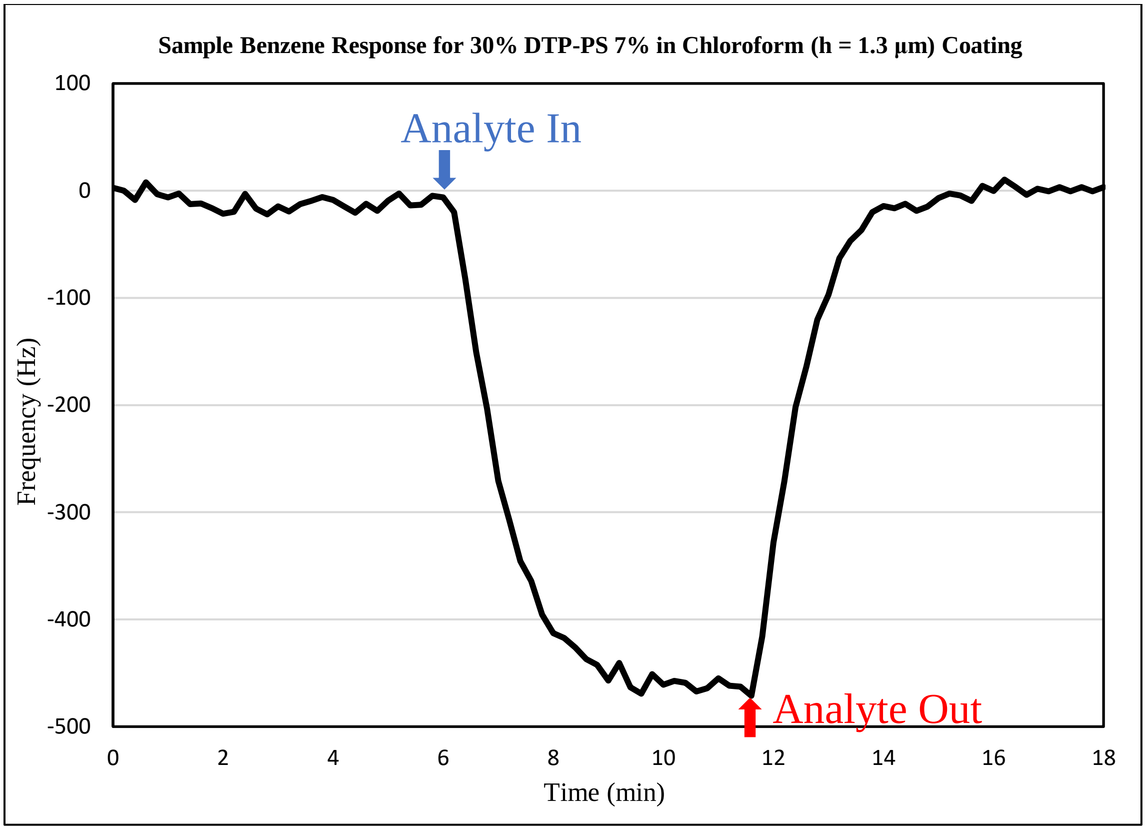

Figure 4. 2: Sample response of 1 ppm Benzene measured by SH-Saw device coated with 30% DTP-PS (h = 1.3µm). Indicated by the blue and red arrows are where analyte is introduced to the coating (absorption) and when the coating is again exposed to DI water (desorption).

Coating responses to BTEX analytes and independent measurement of concentrations are performed according to the procedures outlined in chapter 3. Responses for each coating are collected until a poor signal-to-noise ratio is observed. Based on previous experience, coatings are no longer used once the insertion loss exceeds -35dB because this usually indicates a poor signal-to-noise ratio in the sensor response. For each coating, many measurements with all BTEX compounds have been made. This is done in order to calculate average sensitivity values for each coating to each BTEX compound.

Following response collection, each curve is fit using an exponential curve-fitting program to extract equilibrium frequency shift and response time constant of each response. Each steady-state frequency shift with measured concentration is plotted to generate a graph of the sensitivity of each coating to each BTEX analyte. An example graph of sensitivity to toluene of a 30% DTP-PS coating is shown in figure 4.3 below.

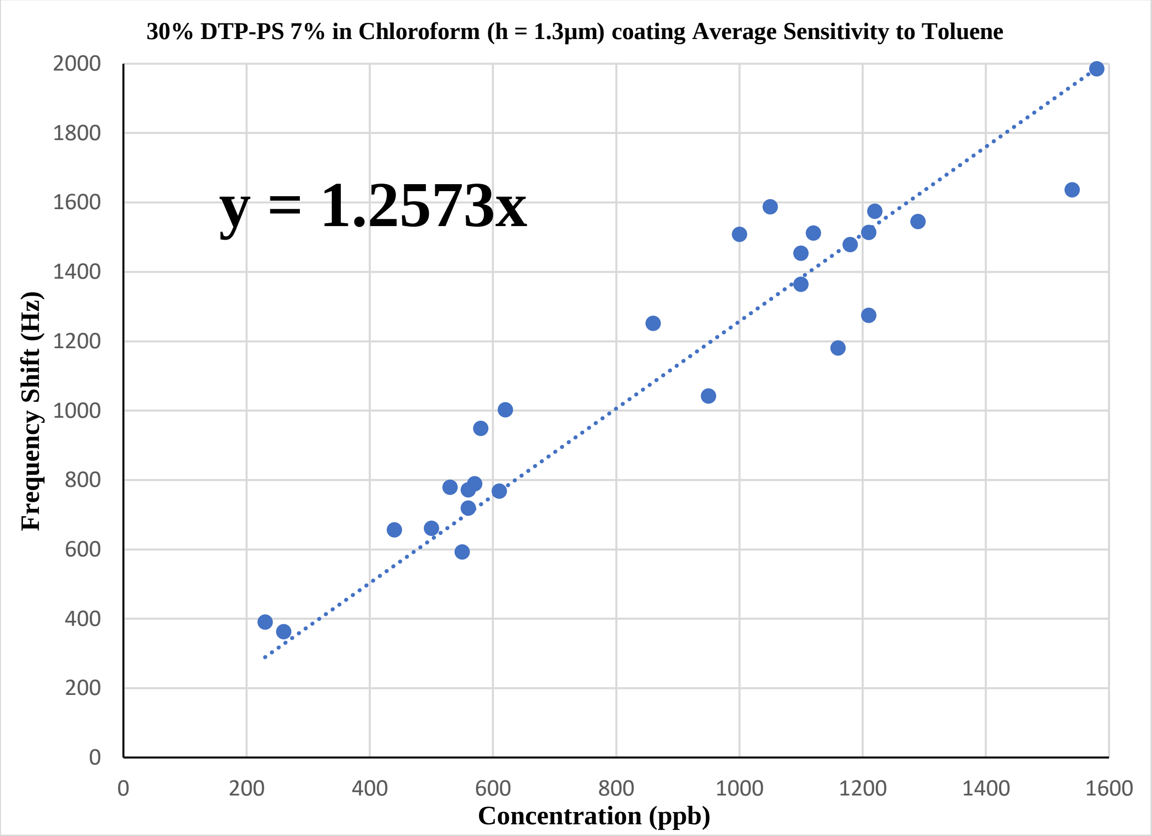

Figure 4. 3: Plot of concentration versus equilibrium frequency shift for responses of 30% DTP-PS coating to varying concentrations of toluene. Measurements were conducted over several weeks/months at varying concentrations and results plotted to obtain sensitivity. Sensitivity as per the slope of this graph is within the calculated standard error for the 30% DTP-PS coating sensitivity to toluene shown in table 4.3 below, indicating that both values are in agreement with one another. Total number of measurement points n in this plot is n = 27.

For every average sensitivity and response time constant presented, standard error has been calculated for the number of measurement responses collected for each coating-analyte pair. Standard error is calculated by using equation 4.1 shown below [68].

$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}} \tag{4.1}$$

In this equation, $\sigma_{\bar{x}}$ is the standard error, σ is the standard deviation, and n is the number of measurements. Number of measurements is varied for each coating-analyte pair, with $10 < n < 40$ for all DTP-PS coatings. A summary of thickness and average sensitivity and time constant for each BTEX analyte with calculated standard error for sensitivity and response time constant are shown in tables 4.3 and 4.4 for each DTP-PS sensor coating.

Table 4.3: Summary of DTP-PS coating thicknesses and sensitivities to BTEX compounds.

Sensor Coating	Thickness (µm)	Benzene Sensitivity (Hz/ppm)	Toluene Sensitivity (Hs/ppm)	Ethylbenzene Sensitivity (Hz/ppm)	Xylenes Sensitivity (Hz/ppm)
22% DTP-PS 6.5% in Chloroform	1.3	250 ± 10	830 ± 50	2470 ± 300	4220 ± 480
30% DTP-PS 7% in Chloroform	1.3	490 ± 30	1220 ± 50	2680 ± 200	5650 ± 480
32% DTP-PS 7% in Chloroform	1.3	520 ± 20	1390 ± 40	3520 ± 230	5680 ± 730
33.5% DTP-PS 7% in Chloroform	1.3	510 ± 20	1390 ± 30	3820 ± 190	5140 ± 400
35% DTP-PS 7% in Chloroform	1.3	530 ± 30	1370 ± 50	2930 ± 130	5080 ± 310

Table 4.4: Summary of response time constants of DTP-PS coatings for BTEX compounds.

Sensor Coatings	Benzene Time Constant (seconds)	Toluene Time Constant (seconds)	Ethylbenzene Time Constant (seconds)	Xylenes Time Constant (seconds)
22% DTP-PS 6.5% in Chloroform	74 ± 6	144 ± 4	365 ± 9	424 ± 7
30% DTP-PS 7% in Chloroform	46 ± 3	125 ± 5	311 ± 22	430 ± 8
32% DTP-PS 7% in Chloroform	38 ± 2	108 ± 3	336 ± 9	407 ± 17
33.5% DTP-PS 7% in Chloroform	42 ± 3	125 ± 4	338 ± 28	430 ± 11
35% DTP-PS 7% in Chloroform	48 ± 3	127 ± 3	366 ± 23	410 ± 22

4.2.3 Definition of Sensor Arrays

Three sensor arrays have been created for analysis in this work. Each array consists of five individual sensor coatings and has been created with a specific goal in mind. Array 1 has been created to observe the behavior and characteristics of an array composed entirely of polymer-plasticizer blend sensor coatings. The goal of this array is to determine if sufficient partial selectivity to BTEX analytes can be achieved with maximum array sensitivity. Coating compositions in this array include 17.5% DIOA-PS, 23% DINCH-PS, and 22%, 30%, and 32% DTP-PS.

Array 2 has been selected to determine the feasibility of creating a sensor array using coatings made only from a single polymer-plasticizer pair with varied mixing ratios. The goal of analysis of this array is an extension of the goal of array 1. If sufficient partial selectivity can be achieved using all polymer-plasticizer blend coatings, partial selectivity of an array of coatings created from a single polymer-plasticizer pair is also of interest. This array includes all DTP-PS coatings presented in this work.

Array 3 has been selected to maximize chemical diversity of the coatings in the array. The goal of this array is to determine if there is a direct link between high chemical diversity of coatings and partial selectivity of an array constructed from these coatings. Coatings for this array are chosen to maximize chemical diversity by selecting coatings with unique compositions. 2.5% PIB, 4% PECH, 17.5% DIOA-PS, 23% DINCH-PS, and 32% DTP-PS coatings have been selected to maximize chemical diversity while still maintaining modest sensitivity to BTEX analytes.

4.3 Comparison of Sensor Arrays

4.3.1 Sensor Array 1

Sensor array 1 shows high sensitivity to BTEX analytes as would be expected from the individual polymer-plasticizer blend coatings. 17.5% DIOA-PS shows the highest sensitivity for toluene and xylenes. 32% and 33.5% DTP-PS account for the highest sensitivity benzene and ethylbenzene respectively. Normalized sensitivity of each coating to each BTEX analyte is shown for analysis of partial selectivity in figure 4.4. This chart acts as a selectivity fingerprint for this array of coatings.

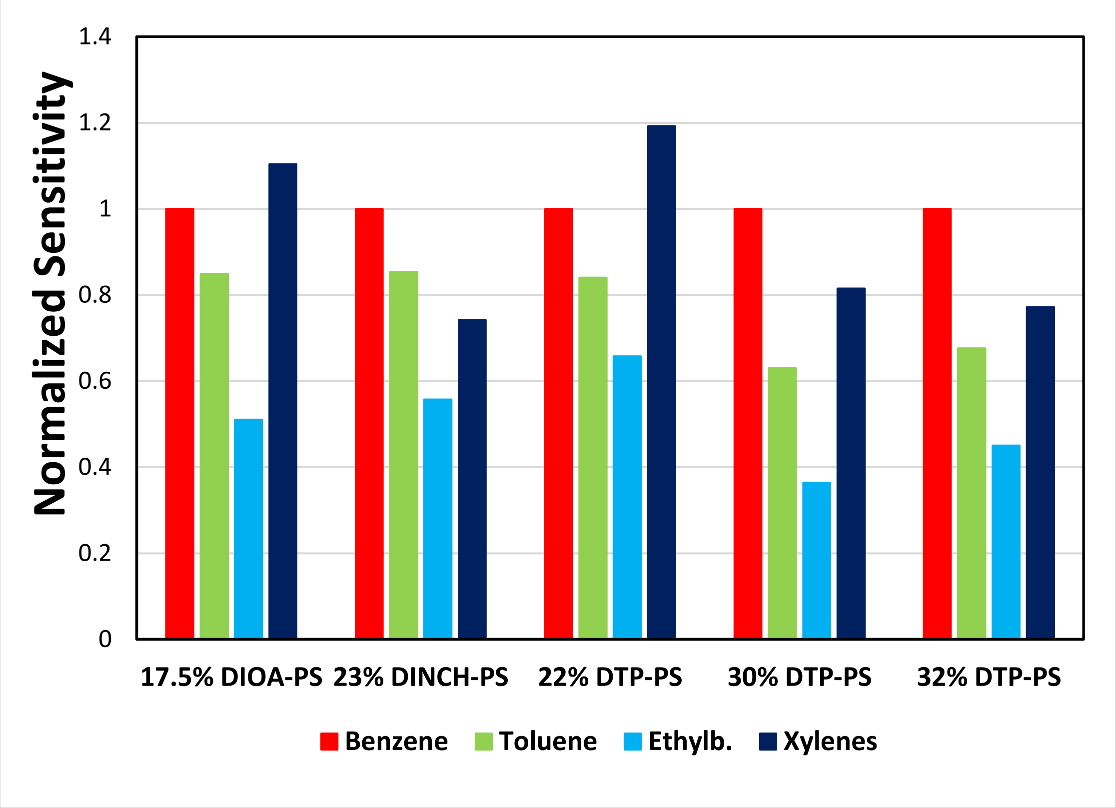

Figure 4. 4: Selectivity fingerprint of array 1.

The purpose of establishing a selectivity fingerprint for the analysis is to visually represent the way in which each coating in the array is sensitive to each target analyte. First, the separation indicated between normalized sensitivities of each analyte for one single coating should be observed. Sufficient separation within the same coating is an indicator of the partial selectivity of that particular coating and is useful in determining selectivity of the array to each BTEX analyte during later analysis. Second, the separation of normalized sensitivities of one single analyte across all coatings used in the array should be observed. This serves as an indicator of the selectivity of the array formed from the coatings presented. Large differences in normalized sensitivities of each coating for one analyte indicates that a unique set of data will be provided by each coating, which will be useful for principal component analysis where unique data sets directly lead to increased selectivity.

With the above points in mind, indicated in this figure is that each sensor in this array has at least one pair of analytes for which normalized sensitivity is significantly different. A large difference in normalized sensitivity across every sensor in an array is necessary for unique identification of BTEX analytes. The bar chart indicates that good selectivity will be seen between benzene, toluene, and ethylbenzene. This is expected as no sensor coatings used in any array presented have shown signs of difficulty in unique detection of these compounds. Partial selectivity of this array to ethylbenzene and xylenes is good, as can be seen in the large differences in normalized sensitivity of each coating except 23% DINCH-PS. This is important as it has not been possible to distinguish chemical isomers ethylbenzene and xylenes using only PIB and PECH in previous work.

The second type of graph used for analyzing arrays in this section are radial plots for each array formed as a visual representation of array selectivity. As described in section 4.1, these plots allow for the easy removal of redundant data. First, the separation and pattern of each analyte sensitivity ratio along a radial axis for a single coating pair should be observed. This can be used to show differences in sensitivity of the coatings, yielding information about the uniqueness of data provided by each coating. Unique data for a given coating implies highly uncorrelated data for the entire array, which will be useful for PCA plots. Second, the pattern of a single analyte for the array using both ratios of sensitivities and response time constants can serve as an indicator of selectivity of the array. The variation between data for the same analyte, as well as the patterns observed for different analytes, can be used to show high or low selectivity. Finally, clear separation of response time constants can provide more uncorrelated data for the array. More separated response time constants result directly in higher selectivity when using multivariate sensing and analysis.

The findings discussed for array 1 are also evident in the radial plot for this array shown in figure 4.5. Time constants and ratios of sensitivities in this array show good separation between benzene and toluene and significant separation between toluene and ethylbenzene. Response time constants shown show good separation of values for DTP coatings. The ratios of sensitivities presented indicate significant variation in data resulting in high selectivity. The ratios of 30% DTP-PS to 22% DTP-PS and 23% DTP-PS to 22% DTP-PS show similar values, but most important for these two ratios is the difference present between ethylbenzene and xylenes. These changes result in increased selectivity to ethylbenzene and xylenes and thus indicate that those two coatings in the array should be kept despite the similar chemical fingerprints observed in figure 4.4. The 23% DINCH-PS and 17.5% DIOA-PS coatings compared with the 22% DTP-PS coating provide unique fingerprints which increase selectivity of the array.

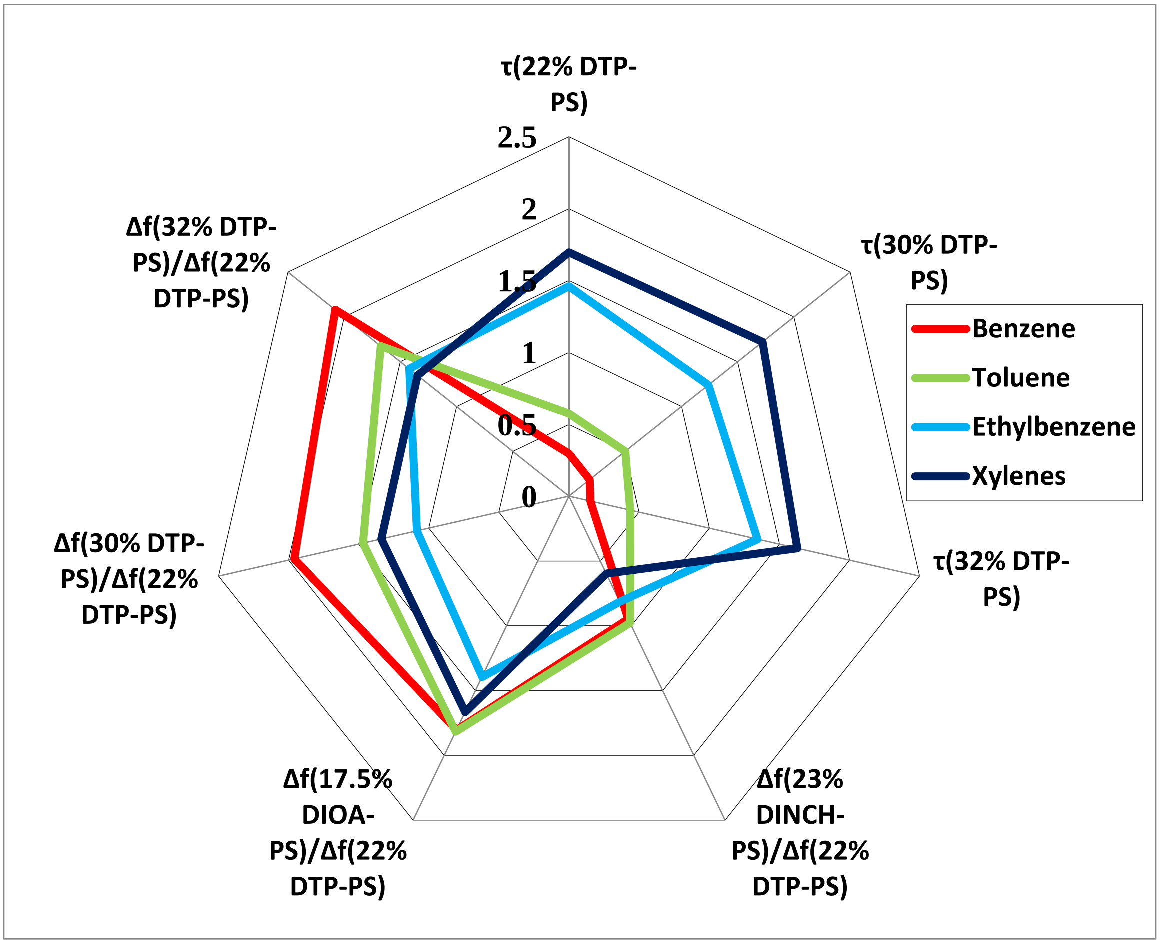

Figure 4. 5: Radial plot showing selected response time constants and ratios of sensitivities of coatings in array 1 (response time constant values divided by 100 for scale).

The final plot formed for each array is a plot of the first two principal components of the data set for each array. After the PCA results have been obtained, these principal components are plotted in a 2-D graph and are used as a direct indicator of selectivity as analyte cluster separation relates directly to array selectivity. Figure 4.6 shows the results of PCA performed for data from sensor array 1. Separation between benzene and toluene clusters is good, as expected based on sensitivity and response time data. Toluene and ethylbenzene clusters are significantly separated. This is also expected, as the time constants of toluene and ethylbenzene show the largest difference in time. Response times for each coating from benzene to toluene to ethylbenzene are approximately 2.75 times larger from one compound to the next. Response time from ethylbenzene to xylenes shows a significantly smaller change. Values are only about 1.2 times larger for all coatings in this array excluding 23% DINCH-PS. The 23% DINCH-PS coating showed no difference in both sensitivity and response time constant between ethylbenzene and xylenes. These reductions lead to the observed reduction in cluster separation despite having similar separation in absolute time to benzene and toluene.

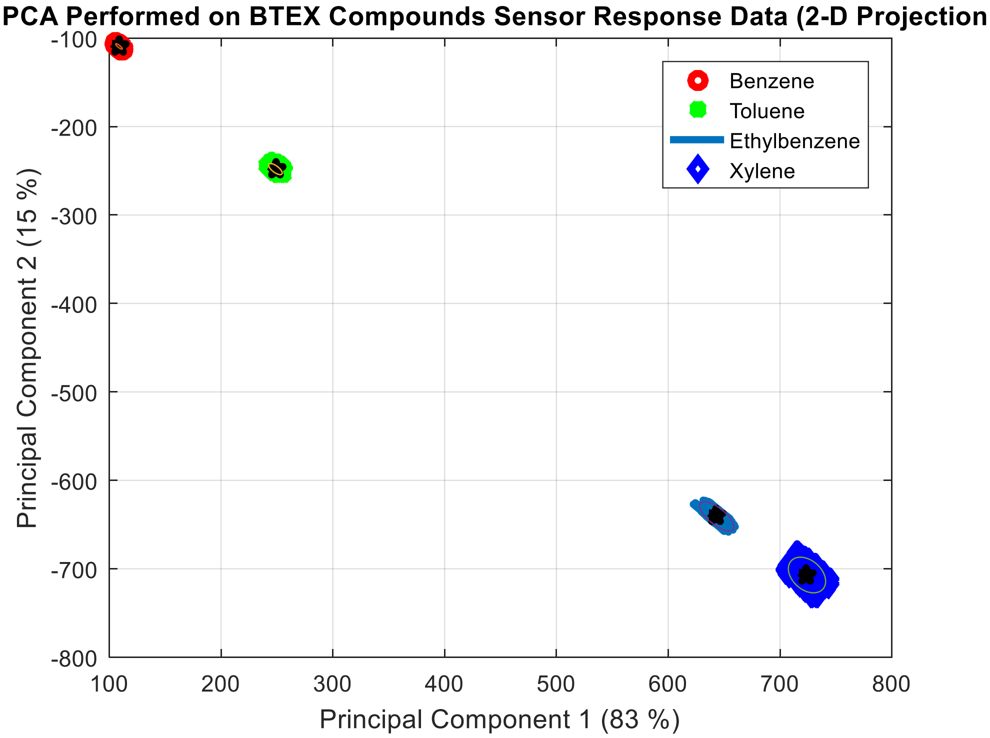

Figure 4. 6: Plot of two-dimensional results of PCA performed for sensor array 1.

4.3.2 Sensor Array 2

The constituent coatings of array 2 have each shown high sensitivity to BTEX analytes, indicating that the array also will have high sensitivity. Analyzing array 2 based on sensitivity data alone indicates that partial selectivity is significantly lower than desired. Calculated average sensitivities to benzene of the 30%, 32%, 33.5%, and 35% DTP-PS coatings are all found to fall within 40 Hz/ppm of one another. These sensitivities all fall within the error margins of the others. For this array, the same observations can be made involving toluene, ethylbenzene, and xylenes as well. The selectivity fingerprint of array 2 is shown in figure 4.7.

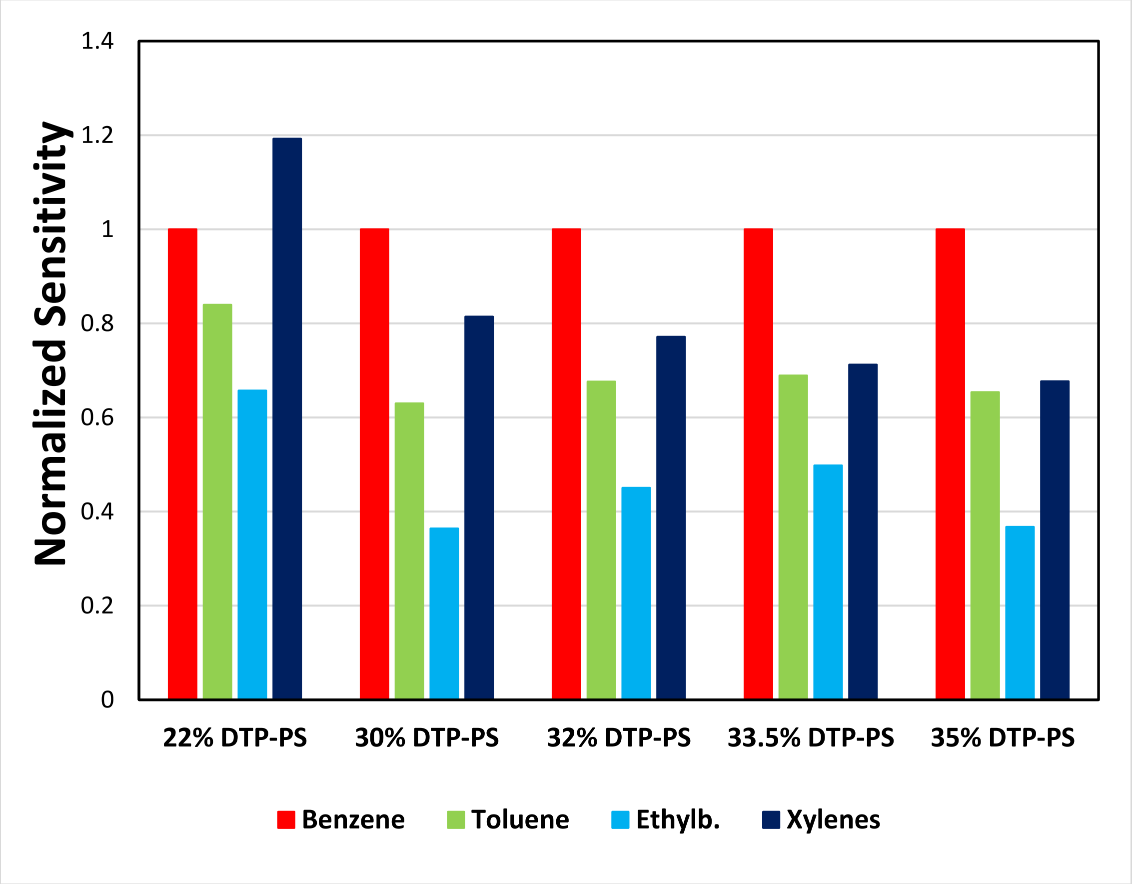

Figure 4. 7: Selectivity fingerprint of array 2.

This selectivity chart indicates that there may not be enough chemical diversity present in array 2 for unique detection of each BTEX analyte. Partial selectivity fingerprints of several sensors in the array are extremely similar to one another. The 30% and 32% DTP-

PS coatings and the 33.5% and 35% DTP-PS coatings are shown to behave almost identically for several analytes.

The incorporation of response time constant into array analysis shows that this array is still selective. Figure 4.8 shows the radial plot of selected time constants and ratios of sensitivities of coatings in array 2 for each analyte. Each coating has a unique time constant for each analyte, and all are well separated from one another. Ratios of sensitivities shown also show several unique variations among coating combinations, though alone they are not significant enough variations to allow for unique detection. The inclusion of time constants is necessary as their use makes up for a lack of chemical diversity.

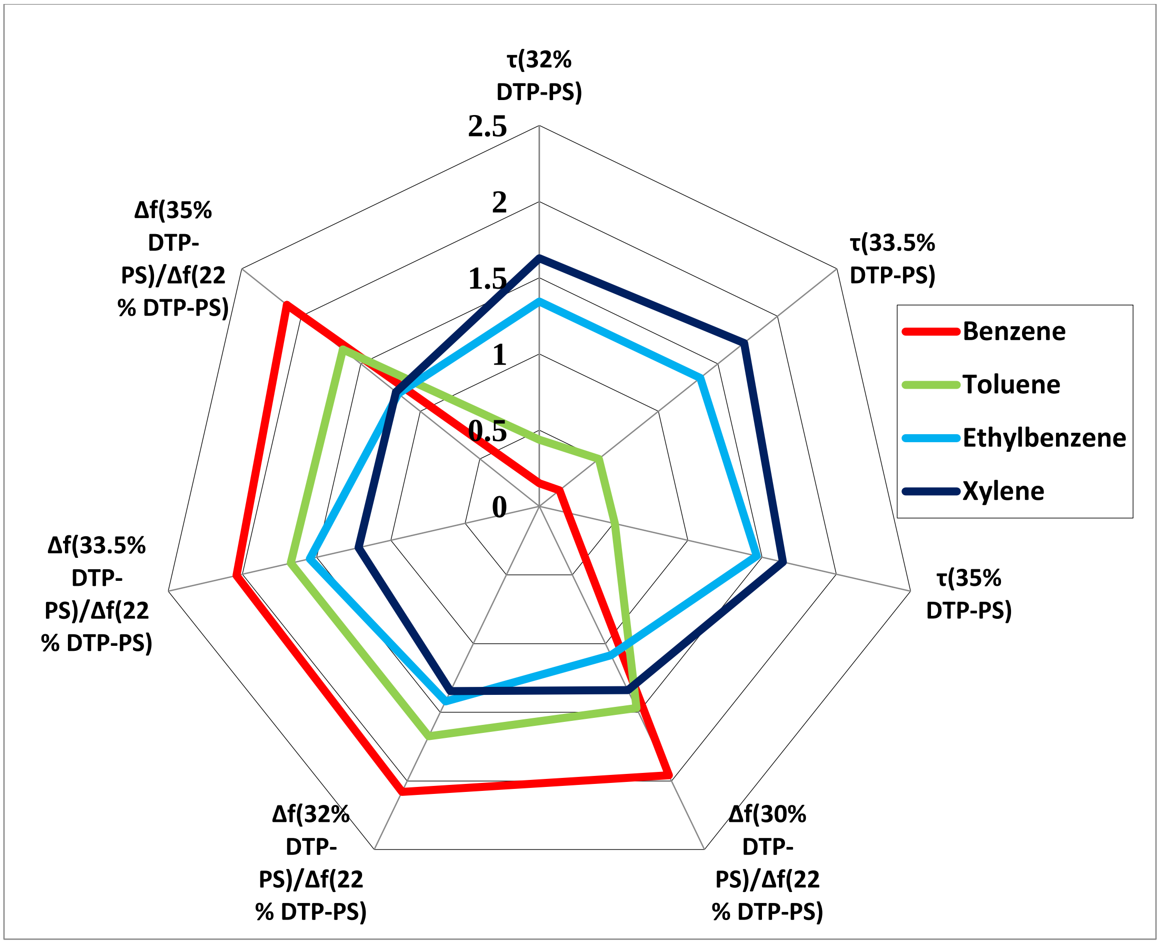

Figure 4. 8: Radial plot showing selected response time constants and ratios of sensitivities of coatings in array 2 (response time constant values divided by 100 for scale).

The results of PCA shown in figure 4.9 confirm that, despite lacking chemical diversity, array 2 is still sufficiently selective with the inclusion of response time constants. The response time constants of this array differ by similar factors as those of array 2 for each BTEX analyte. The exclusion of the 23% DINCH-PS coating in favor of another coating with well separated ethylbenzene and xylene sensitivities and time constants makes use of two additional variables in PCA. This in addition to all time constants of constituent coatings being unique for ethylbenzene and xylenes, which indicates that array 2 shows sufficient selectivity for unique identification of all BTEX compounds.

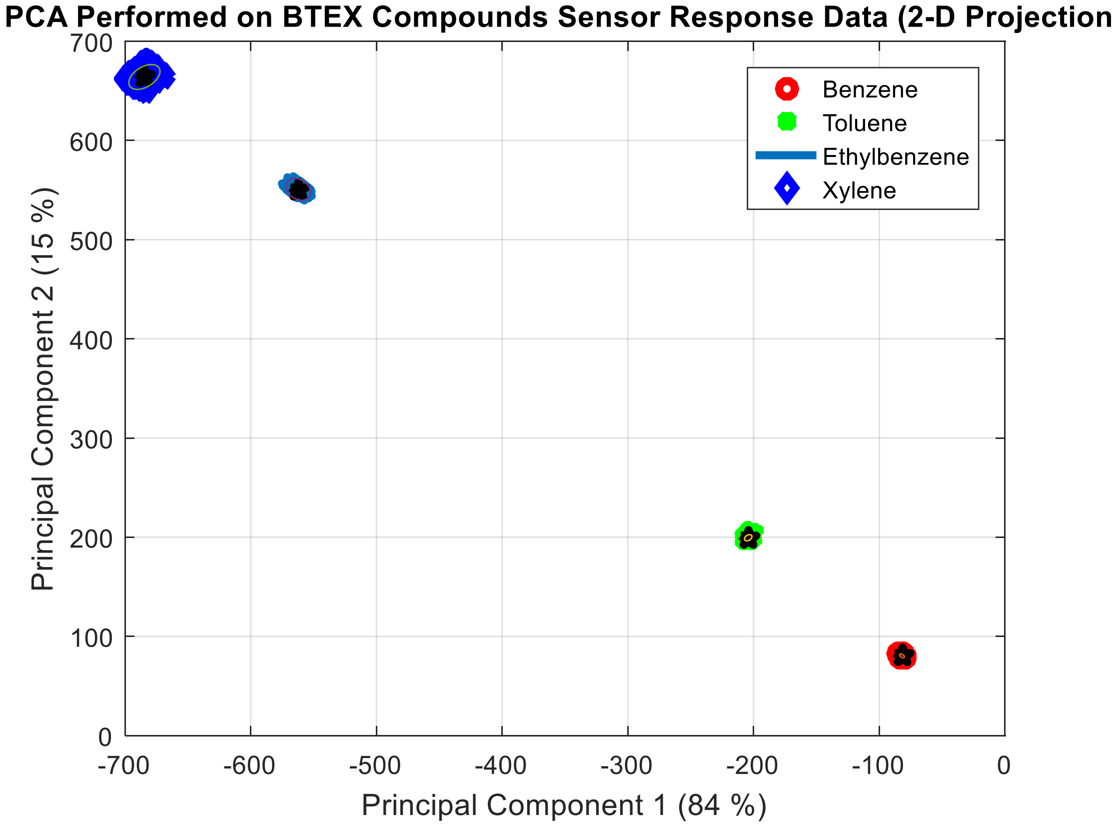

Figure 4. 9: Plot of two-dimensional results of PCA performed for sensor array 2.

4.3.3 Sensor Array 3

Sensor array 3 displays reduced sensitivity with the inclusion of 2.5% PIB and 4% PECH coatings. These coatings increase chemical diversity of the array but come with significant drawbacks. As discussed previously, coatings made from PECH and PIB are unable to distinguish between the chemical isomers ethylbenzene and xylenes. In addition, these coatings also show significantly lower sensitivity than the rest of the coatings used in this work. This results in reduced sensitivity to BTEX analytes in array 3 as well as difficulty in distinguishing between ethylbenzene and xylenes. Figure 4.10 shows the selectivity fingerprint for each coating in array 3. Selectivity between benzene, toluene, and ethylbenzene are very good for this array, as a diverse assortment of sensitivity and response time values are present for each analyte and coating. Unique detection of ethylbenzene and xylenes is difficult using this array, as the partial selectivity indicates that three of the five used coatings show little differentiation between these analytes. Sensitivity and response time data also confirms the above statement, as 2.5% PIB, 4% PECH, and 23% DINCH coatings have very similar or identical values for ethylbenzene and xylenes.

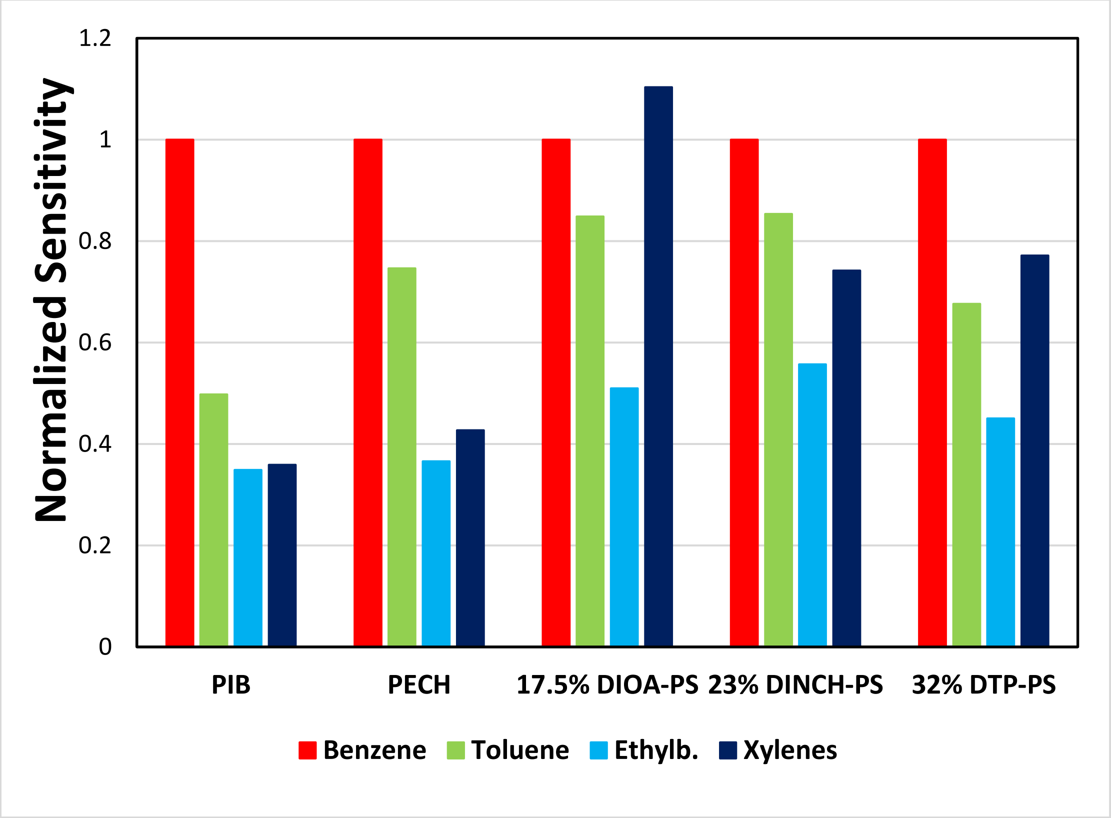

Figure 4. 10: Selectivity fingerprint of array 3.

Shown in figure 4.11 is the radial plot of time constants and ratios of sensitivities for array 3. This figure again depicts the problem present in array 3. Overlapping time constants for 2.5% PIB, 4% PECH, and 23% DINCH-PS coatings in this array indicate that it will be unable to distinguish ethylbenzene from xylenes despite the array having two coatings which can uniquely detect the two analytes on their own. In addition to this, ratios of sensitivities are also significantly less varied than those of the previous two arrays. This could be due to the lower sensitivity of some coatings in this array resulting in ratios of those lower sensitivities being less separated providing lower selectivity to the array. PCA confirms this observation as is shown in figure 4.12.

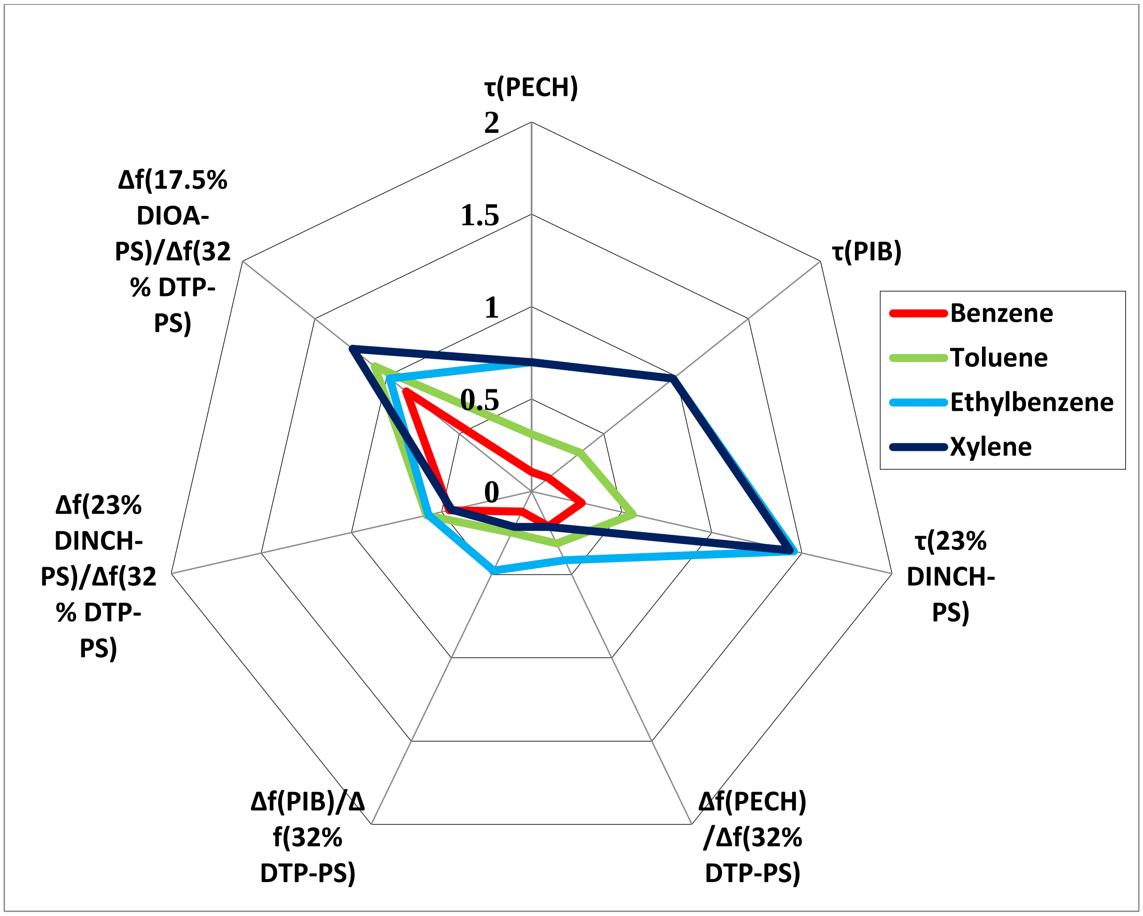

Figure 4. 11: Radial plot showing selected response time constants and ratios of sensitivities of coatings in array 3 (response time constant values divided by 100 for scale).

Results of PCA performed for sensor array 3 shown in figure 4.12 show a clear lack of separation of clusters representing ethylbenzene and xylenes. The lack of separation between ethylbenzene and xylenes clusters indicates lack of selectivity between these two analytes and supports the analysis above.

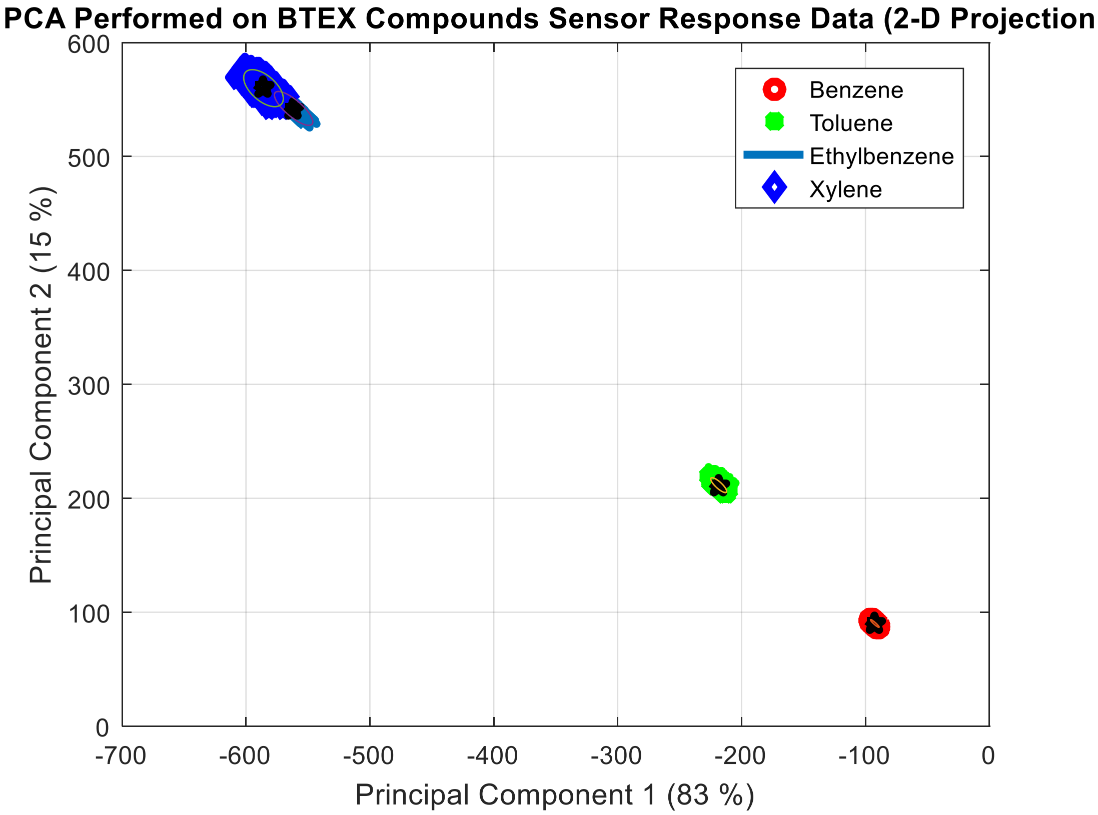

Figure 4. 12: Plot of two-dimensional results of PCA performed for sensor array 3.

4.4 Comparison of Sensor Arrays

4.4.1 Sensitivity Comparison

Sensitivity of the investigated sensor arrays depends on the sensitivity of the constituent coatings. Arrays 1 and 2 include only polymer-plasticizer blend coatings and showed high sensitivity as a result. The inclusion of PECH and PIB coatings in array 3 resulted in a reduction in sensitivity when compared to arrays 1 and 2. Arrays 1 and 2 contain three of the same coatings. To determine which array is more sensitive the remaining two coatings are compared. The sensitivities of these four coatings can be seen in table 4.5 for direct comparison. The sensitivity of the 33.5% DTP-PS coating to xylenes is 5140 Hz/ppm, which is significantly higher than that of the 23% DINCH-PS coating. The 35% DTP-PS coating is slightly more sensitive to benzene than the 17.5% DIOA-PS coating, but the opposite is true for toluene and ethylbenzene. The 17.5% DIOA-PS coating is significantly more sensitive to xylenes than the 35% DTP-PS coating is, with a difference of almost 2000 Hz/ppm. Array 1 is slightly more sensitive to toluene, ethylbenzene, and xylenes than array 2, and array 2 is slightly more sensitive to benzene than array 1.

Table 4.5: Sensitivities of sensor coatings unique to arrays 1 and 2. (1) and (2) indicate that a coating is used in array 1 and array 2 respectively [37, 54].

Sensor Coating	Benzene Sensitivity (Hz/ppm)	Toluene Sensitivity (Hz/ppm)	Ethylbenzene Sensitivity (Hz/ppm)	Xylenes Sensitivity (Hz/ppm)
(1) 17.5% DIOA-PS 11.5% in THF	450 ± 50	1510 ± 200	3450 ± 500	7030 ± 700
(1) 23% DINCH-PS	240 ± 30	810 ± 50	2010 ± 500	2520 ± 250
(2) 22% DTP-PS 6.5% in Chloroform	250 ± 10	830 ± 50	2470 ± 300	4220 ± 480
(2) 35% DTP-PS 7% in Chloroform	530 ± 30	1370 ± 50	2930 ± 130	5080 ± 310

4.4.2 Selectivity Comparison

Each array presented shows sufficient selectivity to benzene and toluene. Significant variations in sensitivities and time constants among constituent coatings show that each array is capable of unique detection of benzene and toluene. PCA results presented in figures 4.6 (array 1), 4.9 (array 2), and 4.12 (array 3) show no overlap in analyte clusters for benzene and toluene, further indicating that unique detection of these analytes is possible using all three arrays.

Significant differences in selectivity are found between ethylbenzene and xylenes for each array. The inclusion of 23% DINCH-PS, 2.5% PIB, and 4% PECH coatings in array 3 and the 23% DINCH-PS coating in array 1 reduce selectivity between ethylbenzene and xylenes for each array. PCA results show that the largest separation for ethylbenzene and xylenes clusters is found in array 2. Each coating in this array provided a unique average sensitivity and response time for both analytes (see tables 4.3 and 4.4 and figure 4.9). Despite the coatings possessing the lowest chemical diversity, array 2 shows the highest selectivity between ethylbenzene and xylenes.

Array 1 is only slightly less selective with respect to ethylbenzene and xylenes. The 17.5% DIOA-PS coating has the highest average sensitivity to and longest response time constant for xylenes. With this coating and three highly sensitive DTP-PS coatings each with unique response time constants, array 1 is still able to maintain selectivity between ethylbenzene and xylenes.

Array 3 shows no selectivity between ethylbenzene and xylenes despite including 17.5% DIOA-PS and 32% DTP-PS coatings which can distinguish between the two analytes on their own. Figure 4.12 shows significant overlapping of ethylbenzene and xylenes clusters in PCA results, indicating lack of selectivity of this array to the two analytes. These results show that the inclusion of PECH and PIB sensor coatings, while increasing chemical diversity for the elements of array 3, yields a significant reduction in selectivity of the array as a whole.

4.4.2.1 Time Constant

A significant factor in determining the selectivity of each presented sensor array is the response time constant of each coating to each analyte. Using exponential curve fitting of single analyte sensor responses to BTEX compounds, both equilibrium frequency shift and response time constant were extracted. The benefit of using multivariate sensing parameters is clearly shown in the results of array 2. Based solely on average sensitivity of each sensor coating in array 2, selectivity would be insufficient for unique detection of all BTEX analytes. The inclusion of response time constants in the analysis shows array 2 to be sufficiently selective to all tested analytes.

Response time constant is also shown to play an important role in explaining why array 3 lacks selectivity for ethylbenzene and xylenes. The results of PCA rely on the degree of uncorrelation present in the correlation matrix of the formed data set. When data used for PCA is highly correlated, the resulting principal components will not show adequate separation. This is the case with the sensitivities and response times of 23% DINCH-PS, 2.5% PIB, and 4% PECH sensor coatings. Utilizing two parameters from each sensor response and including coatings which have distinct average sensitivities and time constants for all analytes under test are highly important in determining array selectivity.

5 SUMMARY, CONCLUSIONS, AND FUTURE WORKS

5.1 Summary

The goal of this work was to implement and analyze sensor arrays made from polymer-plasticizer blend sensor coatings with respect to sensitivity and selectivity to BTEX compounds in liquid environments. Results presented in chapter 4 indicate that each of the three proposed sensor arrays implemented in this work is capable of unique detection of some BTEX compounds with moderate to high sensitivity. Two of the arrays presented, each formed entirely from polymer-plasticizer blend sensor coatings, show high sensitivity to BTEX and are capable of unique detection of each BTEX compound. Coatings, which have been previously investigated include PIB, PECH, DIOA-PS, and DINCH-PS coatings [37, 54, 66]. New coatings investigated in this work include all coatings using the plasticizer DTP. All coatings were tested to obtain multiple responses to single analyte solutions of each BTEX compound. Steady-state frequency shift and response time constant were extracted from each response and were used to analyze partial selectivity of each coating in the array to BTEX compounds.

The motivation for this research was presented with a discussion on the health hazards of BTEX compounds and the low maximum contamination limits set for these compounds. A brief introduction to chemical sensing was discussed and sensors which are commonly used for chemical sensing were presented. Optical sensing techniques and acoustic wave devices were discussed as common sensing platforms, with the focus narrowed to shear-horizontal surface acoustic wave (SH-SAW) devices which were selected for their good performance in liquid phase. SH-SAW devices must be coated with a chemically sensitive film to be used as a sensor. This work used polymer and polymer-plasticizer blends, and the properties affecting coatings made using these materials were discussed. Polymer properties including free-volume and glass transition temperature and plasticizer properties such as compatibility, efficiency, and permanence were discussed to describe selection of coating components. Hansen solubility parameters were used to calculate RED values for coating components and analytes to determine compatibility between polymer, plasticizer, and solvent or between coating component and analyte.

The coatings used to implement the arrays in this work utilize a variety of compositions. Polymer coatings made from PECH and PIB and polymer-plasticizer blend coatings made from DIOA and DINCH plasticizers and PS polymer were designed and tested previously. Polymer-plasticizer blend coatings made with DTP plasticizer and PS polymer were obtained to ensure consistent thickness across all coatings before measurements were performed. Detailed experimental procedures from all aspects of device preparation, coating preparation, device cleaning and spin coating to analyte solution preparation, sensor measurement, and data processing are given in chapter 3.

Measurements were performed and equilibrium frequency shift and response time constant from each sensor response were extracted. Frequency shifts were normalized to 1 ppm analyte concentration and used to calculate average sensitivity for each coating to each BTEX analyte. Average response time constant for each coating to each BTEX analyte was calculated from extracted response time constants.

Average sensitivities and response time constants were used to produce plots and graphs used to analyze each array with respect to sensitivity and selectivity. Sensitivity of each coating to each BTEX analyte was normalized with respect to analyte molecular weight, analyte solubility in water, and 1 ppm benzene. Normalized sensitivities for each coating were plotted in bar graphs to create selectivity fingerprints for each array. Response time constants and ratios of sensitivities were plotted radially to visualize array selectivity in a convenient manner. Average sensitivities and average response time constants with calculated errors for each coating to each BTEX compound were used as input data sets for principal component analysis. The resulting principal components of the data sets were plotted with clusters indicating each BTEX analyte for selectivity analysis.

5.2 Conclusions

Sensor arrays 1, 2, and 3 have each been investigated with particular goals in mind. Array 1 has been investigated to analyze the possibility of creating sensor arrays from only polymer-plasticizer blend sensor coatings, and is composed of 17.5% DIOA-PS, 23% DINCH-PS, 22% DTP-PS, 30% DTP-PS, and 32% DTP-PS coatings. Array 2 has been investigated to determine if good selectivity can be achieved with coatings created from a single polymer-plasticizer pair and is composed of all DTP-PS coatings presented in this work. Array 3 has been formed to provide maximum chemical diversity, and is composed of 2.5% PIB, 4% PECH, 17.5% DIOA-PS, 23% DINCH-PS, and 32% DTP-PS coatings.

Sensor array 1 showed high sensitivity to BTEX compounds. 17.5% DIOA-PS, 30% DTP-PS, and 32% DTP-PS coatings all show extremely high sensitivity to BTEX compounds, contributing significantly towards this array’s high sensitivity. Partial selectivity of the coatings in this array were significantly varied, and PCA results indicate sufficient cluster separation for unique detection of each BTEX compound. These results indicate that highly sensitive arrays with good selectivity made up of polymer-plasticizer blend coatings can be formed provided the coatings are properly selected.

Sensor array 2 looks to extend the findings of array 1 onto an array with constituent coatings made from a single polymer-plasticizer pair with a varied mixing ratio. This array showed high sensitivity to BTEX compounds; however, without the use of the response time constant data, the array lacked selectivity. The inclusion of time constant data in principal component analysis shows that selectivity is sufficient for unique detection of each BTEX compound. Using both sensitivity and time constant data for each analyte-coating pair provides sufficient selectivity to show that arrays of single polymer-plasticizer pairs are feasible, provided that the coatings show unique time constants for each analyte.

Sensor array 3 was formed from both commercially available polymer coatings and polymer-plasticizer blend coatings and shows modest sensitivity to BTEX compounds but lacks selectivity. Coatings made from PECH, PIB, and DINCH-PS are unable to distinguish between ethylbenzene and xylenes. This results in the array not being selective between ethylbenzene and xylenes despite the array including two coatings which are able to distinguish between these analytes individually. It is important to note that array 1 includes the same DINCH-PS coating as in this array, but it does not result in a significant reduction in selectivity. This would indicate that the presence of one coating which lacks partial selectivity to ethylbenzene and xylenes does not necessarily result in lower array selectivity. However, arrays containing several coatings which are not partially selective to ethylbenzene and xylenes does result in reduced selectivity. Array 3 contains the most chemically diverse selection of coatings, which provides excellent selectivity between benzene and toluene and toluene and ethylbenzene. However, because three coatings in this array are unable to distinguish between ethylbenzene and xylenes, array 3 shows little selectivity to xylenes, and thus, shows the lowest overall selectivity of the arrays presented in this work.

The analysis of the three implemented arrays and conclusions drawn can be applied to the formation of an array which combines the best qualities of all arrays discussed. A new array could be implemented to take advantage of the analysis performed to select coatings from each array and provide maximum sensitivity and selectivity. For maximum sensitivity, the 17.5% DIOA-PS, 30% DTP-PS, and 32% DTP-PS coatings are selected. Each of these coatings has very high sensitivity to each BTEX compound and shows partial selectivity to ethylbenzene and xylenes. To provide this array with high selectivity, coatings should be selected which show good partial selectivity and chemical diversity. For good array selectivity, in addition to the three coatings already selected, the 22% DTP-PS coating could also be selected. This coating has good sensitivity to BTEX and shows significant partial selectivity to each BTEX compound, making it a good candidate for this final array.

The final coating selected for this array is the 2.5% PIB coating. As previously discussed, chemical diversity in a sensor array is very important to the selectivity of the array. Array 1 shows that the inclusion of coatings which lack partial selectivity to ethylbenzene and xylenes does not affect selectivity of the array provided that appropriate coatings are selected to compensate for the lack of partial selectivity. By including a polymer coating in addition to the four coatings already selected for the final array, chemical diversity can be improved while still maintaining high sensitivity and good selectivity to ethylbenzene and xylenes. A radial plot of selected response time constants and ratios of sensitivities of the final array is shown in figure 5.1 below.

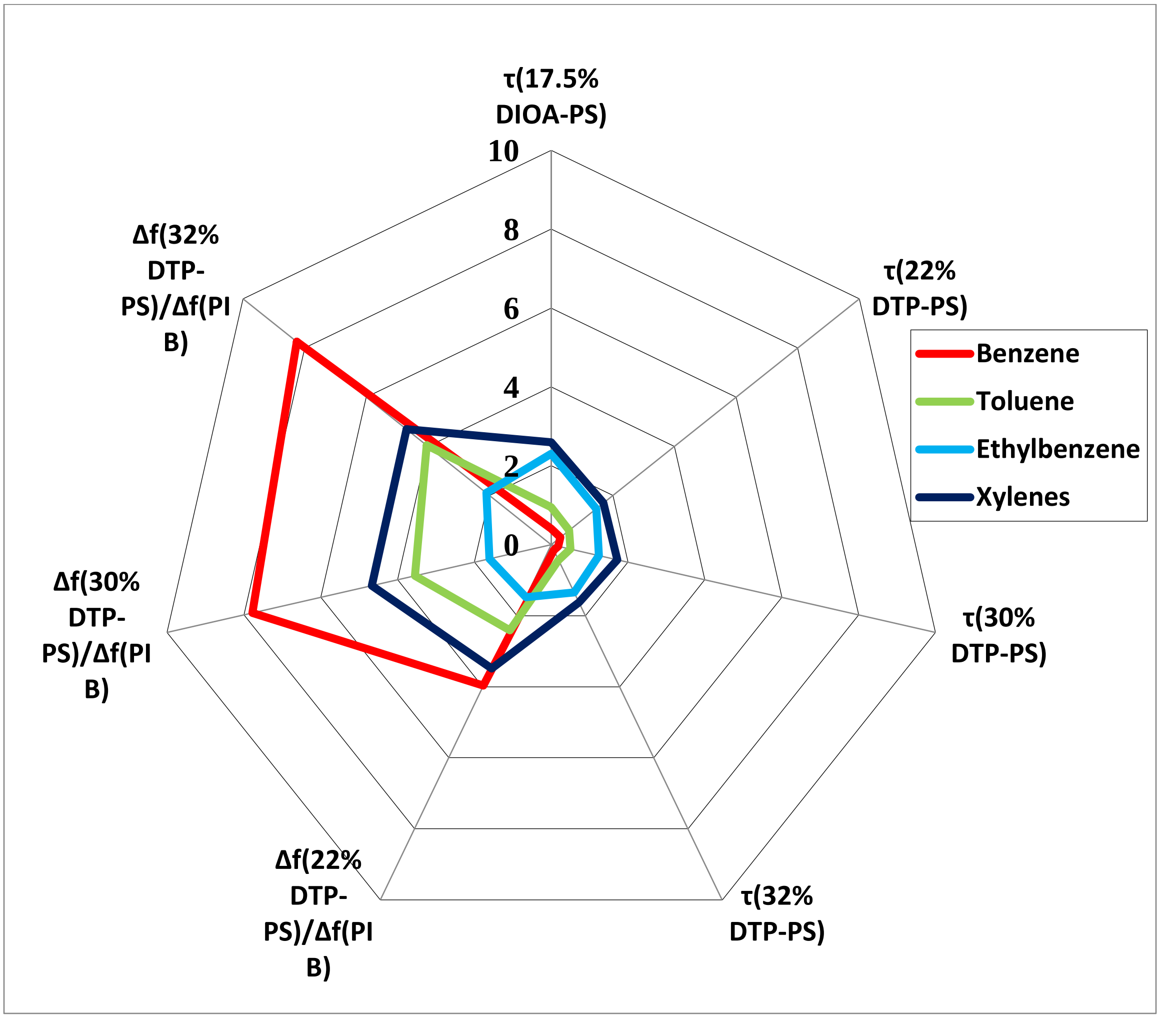

Figure 5. 1: Radial plot of response time constants and ratios of sensitivities for final array. (Response time constant units sec/100).

The plot in Figure 5.1 shows significant separation of ratios of sensitivities and time constants of each coating to each analyte and across all coatings in the array. This variability in values indicates significant selectivity of the array to all BTEX compounds.

PCA confirms that this array shows significant selectivity to all BTEX analytes and results are shown in Figure 5.2.

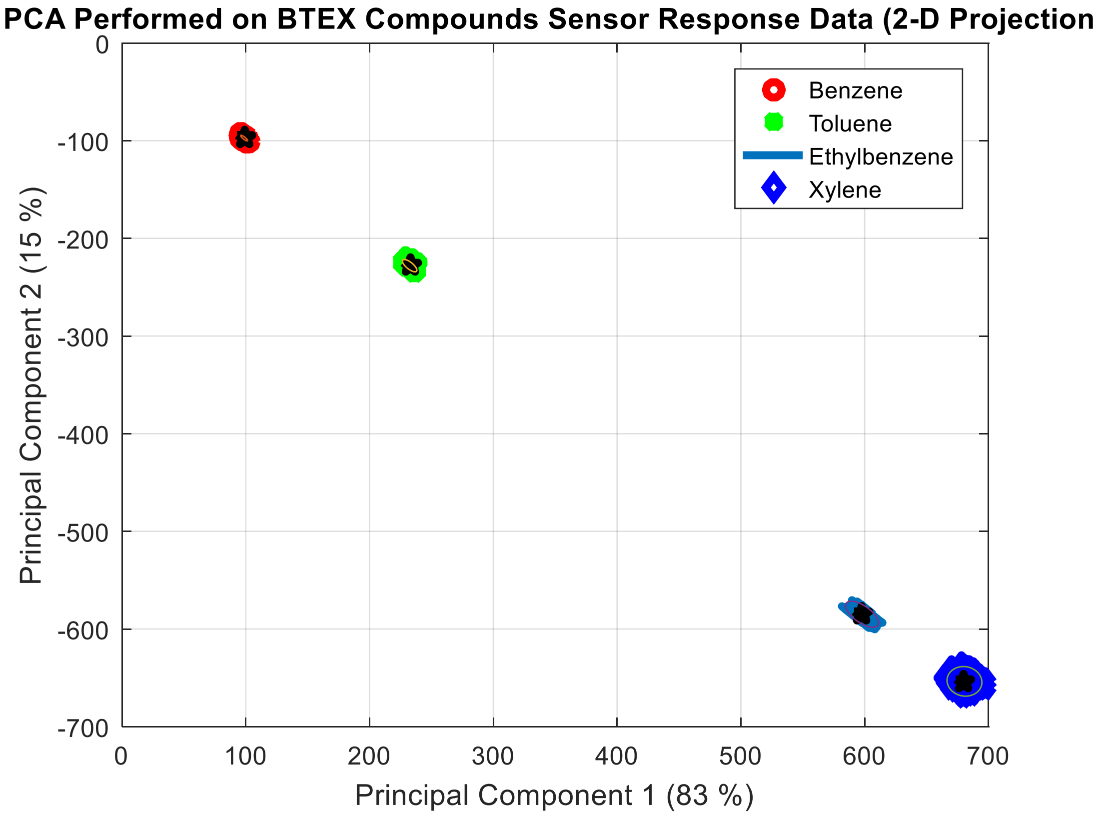

Figure 5. 2: Plot of two-dimensional results of PCA performed for final array.

Selectivity between ethylbenzene and xylenes is sufficient for unique detection and separation is as large as that of arrays 1 and 2. This is due to the inclusion of four coatings with significant sensitivity and good partial selectivity to each BTEX compound. Separation between benzene and toluene clusters is more pronounced than with any of the previous arrays, and the separation between toluene and ethylbenzene clusters is also similar to that of previously presented arrays. This final array will combine the benefits of using a group of highly sensitive and partially selective polymer-plasticizer blend coatings to offset the inclusion of a polymer coating needed for array chemical diversity.

The resulting array shows very high sensitivity to all BTEX compounds and very good selectivity.

5.3 Future Works

To further characterize the sensor arrays presented in this work, individual coatings should be characterized for common interferants. Real world samples will not be simple solutions of one target analyte, but solutions of target analytes and contaminants. Coating characterization for the common interferant 1,2,4-trimethylbenzene (TMB) has already begun. Response time constant for TMB has been observed to be significantly longer than for that of xylenes. More work is still needed in order to obtain average sensitivity and response time constant for TMB. Common interferants such as naphthalene, n-heptane, and others should be investigated.

The arrays formed for this work were designed to show high sensitivity to BTEX while maintaining good selectivity. The weakness of the arrays is that the selected coatings lack enough chemical diversity to provide maximum selectivity, and in order to provide higher sensitivity, some degree of chemical diversity was sacrificed. To solve this problem, new sensor coatings made from polymer-plasticizer blends should be investigated. Developing several new highly sensitive sensor coatings which use a new plasticizer can increase chemical diversity in an array while providing increased sensitivity. New polymers blended with currently used plasticizers can provide another direction of research for increasing the chemical diversity of the coatings of a new array. These coatings could be used to replace one or several coatings in a future proposed array, possibly resulting in higher sensitivity and better selectivity.

Work on the detection of BTEX in liquid phase has been ongoing, but focus is shifting towards new analytes of interest. Detection of pharmaceuticals, antibiotics, and other emerging groundwater/wastewater contaminants using coated SH-SAW devices in liquid phase is of interest. Preliminary work has already begun using polymer-plasticizer blend sensor coatings to detect several antibiotics. Further work is needed to develop sensor coatings which are sensitive to antibiotics.

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