Investigation of the Use of a Plasticizer-Polymer Sensor Coating with Improved Long-Term Stability in the Liquid Phase

Laura Jeanne Alderson
Marquette University

**INVESTIGATION OF THE USE OF A PLASTICIZER-POLYMER SENSOR COATING WITH
IMPROVED LONG-TERM STABILITY IN THE LIQUID PHASE**

By

LAURA JEANNE ALDERSON

**A THESIS SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL,
MARQUETTE UNIVERSITY,
IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTERS OF SCIENCE
(ELECTRICAL AND COMPUTER ENGINEERING)**

Milwaukee, Wisconsin 53233

May 2016

ABSTRACT
INVESTIGATION OF THE USE OF A PLASTICIZER-POLYMER SENSOR COATING WITH
IMPROVED LONG-TERM STABILITY IN THE LIQUID PHASE

LAURA JEANNE ALDERSON

Marquette University, 2016

Benzene is one of the volatile organic compounds present in crude oil and
gasoline. Leakage from underground storage tanks or hazardous waste sites can
introduce benzene contamination into nearby groundwater. Benzene is a known
carcinogen and its exposure is limited by the Environmental Protection Agency to 5
parts per billion (ppb) in drinking water. Early, accurate detection of the presence of
benzene contamination in groundwater supplies is extremely important.

Shear horizontal surface acoustic wave (SH-SAW) devices with a chemically
sensitive coating can be used for the detection of volatile organic compounds in liquid,
such as BTEX (benzene, toluene, ethylbenzene and xylenes). Not all polymers that are
chemically suitable to absorb benzene are able to do so in a reasonable time frame due
to their glassy nature. The polymer is too rigid which does not allow for rapid benzene
absorption. A plasticizer can be added to the selected polymer to lower the glass
transition temperature. This makes the polymer more rubbery allowing for rapid analyte
absorption. However, most plasticizers will tend to leach out of the polymer over time.
The leaching of the plasticizer into the surrounding environment results in an unstable
coating. Without a stable coating, reliable, repeatable measurements are not possible.

It is the intent of this work to use the plasticizer DINCH in the polymer polystyrene to create a stable coating for the detection of BTEX compounds, with the focus on benzene. Various plasticizer concentrations are investigated as well as coating thickness. Sensitivity to benzene and long-term stability of the coating are tested.

ACKNOWLEDGEMENTS

LAURA JEANNE ALDERSON

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1   Introduction

1.1   Problem Statement

The goal of this thesis is to develop a sensor coating for the reproducible and efficient detection of BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) via long-term measurements in the aqueous phase. BTEX are volatile organic compounds (VOCs) that are primarily found in petroleum and its derivatives [1]. These aromatic hydrocarbons find their way into ground water supplies due to accidental releases from storage tanks (underground or above ground), hazardous waste sites, and petroleum production sites. These compounds are hazardous to human health and are therefore highly regulated [2]. Underground water supplies near any storage tank, production site, or other facility that could accidently release these compounds into the surrounding environment are at risk for contamination. Monitoring of these sites for potential spills is extremely important as well as tracking the contamination levels of sites that have been compromised [3].

1.2   Background

The Safe Drinking Water Act, passed in 1974, protects the public's health by ensuring safe public drinking water for America [4]. The Environmental Protection Agency (EPA) limits the exposure of BTEX compounds to humans, as well as many other contaminants in water, by setting a maximum contaminant level (MCL). Out of the BTEX compounds, benzene is considered the most hazardous and has an MCL of 5 ppb (parts

per billion) [5]. Exposure of benzene for a prolonged period of time above this specified level can cause negative health effects such as anemia, blood platelet decrease and an increased risk of cancer [5]. The other compounds have higher MCLs, though they are still hazardous to human health. Toluene is set at 1 ppm (parts per million), ethylbenzene at 700 ppb, and xylenes at 10 ppm [5]. Damage to the nervous system, liver or kidneys can occur with prolonged exposure above the MCLs of these compounds [5]. Because of the extreme limitations and high health risk, there is a greater focus on benzene detection and quantification.

The current method for monitoring underground water supplies is expensive and time consuming. The process currently includes travel of a technician to the site, collection of the ground water sample, preparation of sample, transportation of the sample to a laboratory, and analysis to determine whether any contamination exists and if so, the concentration of the contaminants. The quality of the technician's sampling, preparation and analysis of the sample is extremely important to ensure the chemical composition of the sample is unaltered. These procedures include evacuating the well of stagnant water to allow for the collection of the current groundwater sample, removing the sample from the well (minimizing agitation) into the clean container, properly filling and sealing the container with minimal or no headspace, packaging the sample on ice to minimize volatilization, immediate transportation to a laboratory facility, filtering of the sample to remove unwanted particles (such as sediment) or any other preparation steps for testing (all of which should minimize volatilization) and

finally the testing of the sample (specific to each laboratory) to determine the presence and concentration of BTEX [2].

The expenditure of time and cost of collection, preparation and transportation would be eliminated by use of an on-site chemical sensor or chemical sensor array. A sensor array consists of multiple sensors that produce a different response for the same measurand, resulting in a unique response pattern for each analyte. The sensor system would be accessed remotely and determination of contamination would be concluded quickly. The sensor system would be able to determine the types and concentrations of contaminants in a fraction of the time compared to the current method. Sample testing by the sensor array would be automated to ensure reproducible procedures. Sensor automation eliminates the factor of human error that occurs in sample collection, preparation and analysis. Onsite testing reduces the exposure of the sample to air which decreases the chance of volatilization resulting in a more accurate result.

In the United States, there are currently around 200,000 sites that contain approximately 570,000 underground storage tanks [6], all of which are potential ground water contamination sources. Because of the vast number of sites and the cost of collection and time needed for monitoring each site, not all locations are checked frequently enough to detect a leak before extensive contamination occurs. An on-site chemical sensor system would allow for early, accurate monitoring for the presence of benzene in groundwater supplies as well as an increase in the number of sites tested each year. It would also provide a convenient means to monitor the progress of site remediation once a contaminated site has been identified.

1.3   Chemical Sensor Overview

Sensors are used to detect a chemical or physical phenomenon by the conversion of a chemical or physical parameter into an electrical signal [7]. For chemical sensors, this phenomenon is the presence or concentration of a chemical or molecule. The response of the sensor due to the absorption of the chemical is transformed into a useful analytical signal that can be studied by the user. Typically, the signal measured is electrical, as voltage or current [8]. The change in this electrical signal is due to the presence of a chemical or to a change in the chemical concentration [8]. There may be only one sensor or there may be an array of sensors for more complex data collection. Typically, chemical sensors have a chemically sensitive film that will interact with the chemical(s) of interest. Film choice is application specific and multiple factors are considered, such as chemical(s) to be detected, chemical composition of the film, and solubility between materials.

There are many important parameters that are studied when using chemical sensors, such as sensitivity, selectivity, repeatability, reproducibility, reversibility and response time. Sensitivity of a sensor relates the input quantity to the output electrical signal that is being measured [7]. In chemical sensors, the input quantity is typically the concentration of the chemical of interest. The sensitivity describes the change of the sensor output due to the change in the measured parameter. The change in output of a chemical sensor is contingent upon the interaction between the chemical measurand and the film. Output electrical signal(s) will depend on which type of sensor is used.

Selectivity of a chemical sensor corresponds to how well the sensor can differentiate between various chemicals [9]. Ideally, the perfect chemical sensor would respond to only one chemical and would have no response to others. This ideal case doesn't represent how most chemical sensors respond. Chemical sensors are typically partially selective. In the case of sensors with chemically sensitive coatings, this means that the coating used doesn't interact with just one chemical; it may interact with a number of chemicals. The interaction and absorption of the analyte is dependent on the solubility of the analyte in the liquid or surrounding medium as well as the affinity of the sensor coating for the analyte [10]. The interaction between each chemical and the coating may vary, yielding different response times and sensitivities. Due to partial selectivity, the use of a sensor array becomes important. Use of a sensor array with different coatings allows for the identification and quantification of an analyte in the presence of other chemical contaminants.

Repeatability is also an important sensor characteristic. A good sensor will be able to make repeated measurements on the same day or on different days and produce the same response for the same input. Sensitivities for a chemical should be identical no matter when the data is collected. Repeatability is a requirement for long-term use, in contrast to disposable sensors designed for only a single measurement. Reproducibility of a sensor is the ability to recreate the sensor coating on a different device that yields the same results within error. Repeatability and reproducibility are two different parameters. Repeatability relates to the behavior of one, specific sensor

coating while reproducibility corresponds to the relation between numerous sensor coatings of the same type.

Reversibility of a chemical sensor refers to the sensor's ability to return to its original state or condition before exposure to the chemical. The ability to recover to the original baseline is vital for the repeatability of the sensor. If there is a permanent change to the chemically sensitive coating, the device will not be usable for repetitive or future measurements. The device will have a one-time use and will then need to be replaced, which would be costly and waste valuable time.

Finally, response time of the sensor needs to be considered. Response time of a chemical sensor is the time it takes to reach ninety percent of the steady state response value from the introduction of the analyte sample [10]. Using an exponential fit, the response curve characteristics can be extracted, the total shift (frequency) and time constant of the curve. The time constant and response time are two different parameters. The time constant is defined as the time it takes the sensor to respond the introduction of the analyte, represented as a step input, to reach $\left(1 - \frac{1}{e}\right) \approx 63.2\%$ of the final, asymptotic value for the sensor [11]. The extraction of these parameters will be discussed later in chapter 3. The response time corresponds to the time it takes the analyte to be fully absorbed, to saturation, into the polymer coating. Steady state of the sensor occurs when no more analyte molecules are able to be absorbed into the coating. The sensor should respond in a reasonable amount of time. For the sensor coatings used in this work, typical response times for all the BTEX compounds were

under an hour with benzene being the fastest. Response times differ for various polymer coatings; the response time is dependent on the rigidity and thickness of the coating and is independent of analyte concentration [10]. A thicker coating will result in longer response times due to a larger number of molecules being absorbed to reach equilibrium. Softer coatings result in a faster response time because polymer molecules are more flexible and the migration process of the analyte is less restricted.

1.4   Acoustic Wave Chemical Sensors

Acoustic wave sensors are one of the many commercially available sensors. These types of sensors can be used as both physical and chemical sensors. An acoustic wave propagates in the form of vibration or oscillation in an elastic medium by creating physical deformation along the propagation axis [12]. The speed of the wave propagation is determined by the mechanical properties of the medium material. An acoustic wave device can be used as a sensor by monitoring the characteristics of the acoustic wave as it propagates within the medium. In the presence of an analyte, properties of the sensor coating change. The changes in coating properties affect the characteristics of the propagating acoustic wave such as velocity and amplitude of the wave. The variation in velocity can be monitored by a change in frequency or phase [8], [13].

The substrates used to implement these devices are made of piezoelectric materials such as quartz, lithium tantalate, or lithium niobate. Each piezoelectric material has a different elastic constant, piezoelectric constant and dielectric constant.

These material constants are the properties that must be considered when choosing the substrate material for the acoustic sensor. The propagation of the acoustic wave is generated using the piezoelectric effect. Piezoelectric crystals allow for transduction to occur between electrical and acoustic energy [14]. The piezoelectric effect allows an electric charge to be generated when a mechanical stress is applied as well as the reverse process. The reason this occurs is because the charge centers in the material shift when stress is applied. This creates an external electric field. When the reverse process happens, an electric field causes the material to undergo a deformation [15]. The most common types of acoustic wave devices used for sensing applications include the thickness-shear mode (TSM) resonator, surface acoustic wave (SAW) device, acoustic plate mode (APM), and the flexural plate wave (FPW) [9] and are shown in Figure 1.

Acoustic wave chemical sensors consist of an acoustic wave device made of the chosen piezoelectric material. The sensing surface is coated with a thin, chemically sorptive film that will interact with the chemical of interest. In the presence of the analyte, the film will swell and undergo viscoelastic changes. The film acts as a chemical to physical transducer by conveying the changes of the film due to the analyte to the propagating acoustic wave [14]. The ideal properties of the film and the film chosen will be discussed in further detail in chapter 2.

Figure 1: Four types of acoustic wave sensors. (a) Thickness-Shear Mode (TSM) resonator; (b) Surface Acoustic Wave (SAW) sensor; (c) Shear-Horizontal Acoustic Plate Mode (SH-APM) sensor; and (d) Flexural Plate Wave (FPW) sensor [14].

Figure 1 shows an illustration of each acoustic wave device type previously named. The TSM resonator in Figure 1a, is the oldest acoustic wave device with wave propagation through the bulk of the device. The device is made from a piezoelectric disk with a circular electrode on each side. The TSM resonator, also known as the quartz crystal microbalance (QCM), typically uses quartz as the piezoelectric material for the sensor platform. When an oscillating electric field is applied, the acoustic wave propagation is perpendicular to the surface meaning the wave travels through the bulk of the device. The particle displacement is parallel to the surface [16]. The device will have a specific electromechanical resonance that is due to the shear wave phase velocity in the specific substrate and the thickness of the device [13], [14]. The TSM resonator is typically used for metal or thin film deposition [13], but can also be used as

a chemical sensor when a chemically sensitive film is deposited on the surface [17], [18].

When used as a chemical sensor, the chemically sensitive film absorbs the analyte,

changing the mass of the coating. The film must be sufficiently thin and rigid enough to

move synchronously with the oscillating surface. This mass loading on the surface

affects the resonance of the device. This change in resonance can be correlated to the

concentration of the analyte being detected.

The SAW device, Figure 1b, has a different mode of propagation which is

confined very near to the surface, within one acoustic wavelength [12], [14], [19]. This

propagation mode was discovered by Lord Rayleigh in 1885 [19]. These Rayleigh waves

consist of coupled compressional and shear vertical waves causing the particles at the

surface to follow an elliptical path [14]. When a sensing layer is put on the surface of the

device, acoustic wave energy from the substrate couples with this surface layer.

Acoustic energy at the surface of the device allows for higher sensitivity to surface

perturbations such as mass loading or other changes in the sensing layer's properties.

Typically, the SAW devices consist of a delay line with two interdigital transducers (IDT).

One IDT is used to generate the surface acoustic wave by supplying an oscillating electric

field. The SAW travels across the delay line where it is received by the other IDT. This

IDT takes the mechanical motion from the propagating acoustic wave and converts it

into an electrical signal [12]. The performance of the acoustic wave, and therefore the

sensor, depends on the length, width, position and thickness of the IDT [13].

SAW devices have a surface-normal displacement at the boundary of the

device's surface. This allows for loss of acoustic energy to the surrounding environment

when in a liquid environment. In this specific application, the energy couples into the

liquid producing compressional waves. This loss of energy causes extreme attenuation

of the acoustic wave within the solid [14]. For this reason, the SAW device is not suitable

for liquid sensing applications.

A subset of the SAW device is the shear horizontal surface acoustic wave (SH-

SAW) device with no vertical particle displacement component. The shear horizontal

wave occurs with the proper cut of the rotated piezoelectric crystal [13]. The

piezoelectric crystal material and orientation are such that only the SH-SAW with no

vertical component of the particle displacement is excited by the transducer. With no

particle displacement in the vertical plane, energy does not create compressional waves

in the surrounding aqueous environment making the SH-SAW device ideal for chemical

liquid sensing applications [9], [20], [21]. The SH-SAW device will be the basis for the

sensor work described in this thesis. Further detail about the characteristics of the SH-

SAW device will be discussed in section 1.5.

The APM device, Figure 1c, looks similar in appearance to the SAW device. It has

two IDTs for acoustic wave generation and reception. The difference between the APM

and SAW device is in the type of acoustic wave propagation. The acoustic wave in an

APM device propagates through the bulk of the device. The acoustic energy is confined

between the upper and lower surface of the device by reflections at the boundaries. The

thickness of this device dictates the sensitivity to surface perturbations. Though the

APM device does not have as high sensitivity to surface changes compared to the SAW

device, it does have one extra advantage. Because the acoustic wave interacts with the

upper and lower surface of the device, both of these surfaces can be used for sensing [14].

Finally, for a FPW device, Figure 1d, the acoustic wave propagation occurs in a thin membrane. This device can be used in liquid environments if it is constructed in such a way that the acoustic wave phase velocity is lower than that of the liquid surrounding it. The slow propagation does not radiate any energy into the neighboring liquid keeping the energy within the device [14]. FPW devices also use the same generation and detection of the acoustic wave as the SAW and APM using two interdigital transducers. The downside of the FPW device is that it consists of a thin membrane which is very fragile. This causes the device to be difficult to work with due to the lack of physical robustness.

For the applications investigated in this thesis, the device must operate in an aqueous environment. The SH-SAW device is the most suitable choice as a sensor for this work. The APM has lower sensitivity to surface perturbations compared to the SH-SAW and the FPW is extremely fragile. The TSM resonator also has lower sensitivity compared to the SH-SAW, but may be increased by reducing the thickness for a higher operating frequency. In doing so, the device becomes very thin and fragile [13]. The SH-SAW device was chosen for this application because it is very sensitive to surface perturbations and is fairly robust compared to the other devices.

1.5   SH-SAW as a Chemical Sensor

The SH-SAW device is an ideal platform for a chemical sensor in liquid environments because of the shear horizontal displacement of the acoustic wave. When the SH-SAW device is used as a chemical sensor, a thin, polymer film is deposited on the surface. This film is a chemically sensitive coating that not only interacts with the analytes of interest, but also acts as a waveguide. The acoustic wave in SH-SAW devices propagates deeper in the substrate than a SAW. A coating with lower acoustic shear velocity than the substrate acts as a waveguide and traps the acoustic wave energy closer to the surface, thus increasing the sensitivity. The sensing area of the delay line is metalized and grounded to reduce acoustoelectric interactions between the propagating wave and the liquid [16]. The metalized layer is made of gold which has a slower wave velocity than the LiTaO$_3$ substrate. This also confines the acoustic wave to the surface of the device [22]. The SH-SAW device is used as the sensor platform in this project due to its ability to operate in liquid environments with high sensitivity for chemical sensing applications. Further detail on SH-SAW propagation theory will be discussed in Chapter 2.

1.6   Objective of Research

As discussed previously, the current method for groundwater testing of BTEX contamination is costly and time consuming. There is a need for an in-situ sensor that can monitor the status of the groundwater and detect very low levels of BTEX

contamination. Benzene is the focus due to its extreme health hazards and low limit allowance in groundwater.

There have been previous studies that investigated detection of aromatic hydrocarbon compounds in liquid environments as seen in [10], [22], [23], [24]. These references include various polymer coatings on TSM resonators and SH-SAW devices that show sensitivity to BTEX compounds. Poly (epichlorohydrin) (PECH), poly (isobutylene) (PIB), and poly (ethyl acrylate) (PEA) were found to be suitable candidates for a sensor array. A sensor array would call for a few additional coatings to produce enough partial selectivity and varying sensitivities to the BTEX compounds to accurately detect, differentiate and quantify any analytes in the sample.

Plasticized polymers have been investigated as another type of coating for chemical detection, shown in references [17], [18]. The results found that plasticized polymers can be suitable coatings for chemical sensing. Response characteristics are dependent upon the chosen polymers, plasticizers and concentrations of each. Long term stability of promising plasticizer polymer coatings must be investigated to determine suitability for use in a sensor array.

The focus of this project is to develop a new, partially selective, highly sensitive, reproducible plasticizer-polymer coating for a SH-SAW device for the detection of benzene in an aqueous environment with enhanced long term stability. The proposed sensor coating is a plasticizer-polymer mixture of DINCH (1,2-Cyclohexane dicarboxylic acid diisononyl ester) and polystyrene (PS). Various plasticizer concentrations and coating thicknesses as well as the long term stability of the coatings will be investigated

and discussed. The criteria for the chosen polymer and plasticizer will be discussed in chapter 2.

1.7   Thesis Organization

The thesis will be organized in five different chapters. Chapter one was the introduction. It introduced the problem to be investigated with the background and the current status of sensing methods. A qualitative overview of chemical sensors was provided with further discussion on acoustic wave sensors, focusing on the SH-SAW device. The objective and motivation of this thesis was defined. Chapter two goes into detailed theoretical discussion. Acoustic wave theory is presented with focus on SH-SAW principles. Polymer properties are examined focusing on solubility and material transitions. Various plasticization theories are considered and material choice, stability and effects on sensing are studied. Chapter three offers experimental methods and materials. Detailed steps for preparation and experimental procedures are provided. Chapter four will present experimental results with specific figures and tables. The significance of the experimental results are included and detailed discussion on ideal coating parameters will be provided. And finally, chapter five will include the summary and conclusion of all the work performed. Future work and improvements are suggested and discussed.

2   Theoretical Discussion

2.1   Introduction

The device used in this project was a 36° rotated Y-cut lithium tantalate SH-SAW device. The lithium tantalate substrate was chosen over quartz and lithium niobate because of its inherent properties, specifically, its high dielectric constant [25] which permits immersing the entire polymer-coated device, including the transducers, in water without suffering excessive acoustic-wave loss. The rotational cut of the substrate allows the SH-SAW to be excited and to propagate for use in liquid-phase sensing applications. The schematic of the SH-SAW sensor is shown in Figure 2.

Figure 2: Schematic representation of a guided SH-SAW sensor with a two-ten finger paired IDT pattern (one line only)

The design of the IDT was chosen to be a two-ten finger pattern [26]. The delay line was metalized with gold and grounded to isolate any electrical interaction of the SH-SAW with the surrounding liquid. For chemical sensing, a SH-SAW device is coated with

a chemically sensitive polymer that absorbs the analyte of interest. This absorption results in a surface perturbation that affects the properties of the propagating SH-SAW. There are two types of geometries used for a chemical SH-SAW device, a three-layer or a four-layer geometry. In a three-layer geometry, the chemically sensitive coating also acts as a wave guiding layer to keep the acoustic energy trapped closer to the surface. A four-layer geometry has two layers on top of the substrate. The first layer is the wave guide layer directly on top of the substrate and the second is the chemically sensitive layer that is in contact with the surrounding analyte solution. The three-layer geometry was chosen for this work and can be seen in Figure 3 [27]. The three-layer geometry requires only one coating deposition and characterization. One coating layer requires fewer preparation steps and reduces the error when reproducing the sensor coating on another device.

Figure 3: A general three-layer geometry for an acoustic wave sensor showing the piezoelectric substrate, polymer coating and surrounding liquid with analyte molecules present.

In this chapter, the theory of wave propagation for a SH-SAW device will be reviewed. Properties of the polymer coating will be described as well as the discussion on coating selection criteria. Sensing mechanisms of the coated SH-SAW chemical sensor and the analyte sorption process will be defined.

2.2   Acoustic Wave Theory

As discussed earlier, the SH-SAW propagates across the device from the input IDT to the output IDT with particle displacement parallel to the surface. Because of the piezoelectric nature of the substrate and the piezoelectric effect which translates the electrical input of an oscillating voltage (therefore oscillating electric field) into periodic strain, an acoustic wave is generated. The periodic strain is a mechanical (acoustic) wave that propagates along the device surface in a direction dictated by the crystal cut and orientation [28]. The acoustic wave generated by an AC voltage supplied to the ITDs can be seen in Figure 4. The SAW excited by each IDT finger pair adds to one another [28]. To obtain an efficient coupling between the electrical input and the generated mechanical wave, the periodicity of the IDT, the center-to-center distance between adjacent finger pairs, is matched with the mode wavelength along the surface [14]. As the SAW travels across the device, the wave carries an oscillating electric field. This induces charge in the output IDT, which is then analyzed to determine any change in the signal.

Figure 4: (a) Acoustic wave generation from (b) IDT finger pairs supplied with an AC voltage [14]

The acoustic wave that propagates along the surface of the device is described by the following expression [14],

$$u_2(x_1, x_2, x_3, t) = u_2(x_3, t)e^{j\omega t - \gamma x_1} \quad (1)$$

where x_1, x_2, and x_3 represent coordinate directions shown in Figure 3, ω is the angular frequency ($2\pi f$), and γ is a complex factor described as a function of the attenuation α and wavenumber k of the propagating wave. The expression for γ is

$$\gamma = \alpha + jk, \quad (2)$$

where the wavenumber is given by the angular frequency divided by the wave velocity, $\frac{\omega}{v}$ [14]. When the frequency of operation is constant, changes in the wave propagation can be expressed by a change in attenuation and wave velocity as

$$\Delta\gamma = \Delta\alpha + j\Delta k = \Delta\alpha - jk_0 \frac{\Delta v}{v_0}. \quad (3)$$

In (3), k_0 and v_0 are the unperturbed wavenumber and acoustic wave phase velocity of the system, respectively. This expression is typically normalized by dividing by the unperturbed wavenumber:

$$\Delta\gamma' = \frac{\Delta\alpha}{k_0} - j\frac{\Delta v}{v_0}. \qquad (4)$$

A network analyzer is typically used to monitor the frequency spectrum of the device as it is exposed to the analyte. When the analyte interacts with the film, there is a change in the wave velocity and attenuation. The change in wave velocity is correlated to the change in frequency. When the entire propagation path is perturbed, the normalized change in wave velocity is equal to the normalized change in velocity

$$\frac{\Delta f}{f} = \frac{\Delta v}{v}. \qquad (5)$$

The changes that occur to the velocity and the attenuation are related to changes in mass (m), viscoelastic constant (c), dielectric constant (ϵ), conductivity (σ), temperature (T), or pressure (P). When the perturbation is small, the change in the velocity and attenuation can be expressed as [9]

$$\Delta v = \frac{\delta v}{\delta m}\Delta m + \frac{\delta v}{\delta c}\Delta c + \frac{\delta v}{\delta\epsilon}\Delta\epsilon + \frac{\delta v}{\delta\sigma}\Delta\sigma + \frac{\delta v}{\delta T}\Delta T + \frac{\delta v}{\delta P}\Delta P, \qquad (6)$$

$$\Delta\alpha = \frac{\delta\alpha}{\delta c}\Delta c + \frac{\delta\alpha}{\delta\epsilon}\Delta\epsilon + \frac{\delta\alpha}{\delta\sigma}\Delta\sigma + \frac{\delta\alpha}{\delta T}\Delta T + \frac{\delta\alpha}{\delta P}\Delta P. \qquad (7)$$

The changes are expressed by the partial derivatives with respect to the parameters that affect them. It is shown that the attenuation is not affected by any mass loading of the coating. As seen in equations (6) and (7), there are multiple

parameters that can affect both the velocity and attenuation. Some of these effects can be eliminated or neglected. The grounded metalized delay line, which eliminate any electric field on the propagating path, serves the purpose to eliminate the acoustoelectric interactions. This eliminates the changes due to ϵ and σ. The experimental design is that a constant temperature is maintained during the experiments. However, a thermistor is also used to track any temperature variation that could occur and cause noticeable changes in the response. Lithium tantalate has a temperature frequency coefficient of between -30 ppm/ºC and -40 ppm/ºC for SAW devices [29]. Changes on the order of 10 millidegrees or less will not significantly affect the frequency response of the device. SH-SAW devices are less sensitive to small changes in the ambient pressure due to the particle displacement in the shear horizontal plane [9]. These experimental designs lead to the following simplified expressions for velocity and attenuation change,

$$\Delta v = \frac{\delta v}{\delta m}\Delta m + \frac{\delta v}{\delta c}\Delta c , \qquad (8)$$

$$\Delta \alpha = \frac{\delta \alpha}{\delta c}\Delta c . \qquad (9)$$

The frequency response of the sensor in the presence of the analyte is contingent upon the chemically sensitive coating used. The mass loading and viscoelastic changes to the film are dependent upon the affinity of the analyte being absorbed into the coating. Solubility parameters and partition coefficients must be considered when choosing the ideal film [9], [22].

2.3   Defining Properties and Parameters

2.3.1   Polymer Properties

A polymer is a large molecule made of many atoms that are arranged in a long-chain with a repeating smaller subunits, or monomers. They may be the same monomer repeated or it may be many different monomers repeated within the polymer [30]. Sorbent polymers used for acoustic wave devices sensing applications are usually viscoelastic and undergo shear deformation. The shear modulus of the polymer, *G*, can be used to characterize the polymer as it behaves under a shear deformation. The shear modulus is a complex value described by the storage modulus, *G′*, and the loss modulus, *G″* [9], [20], [22]:

$$G = G' + jG''$$
(10)

The storage modulus represents the energy stored and released as the coating displaces with the SH-SAW. The loss modulus represents the energy lost from the system, typically in the form of heat. As stated in (5), the frequency response due to the analyte is related to the change in wave velocity. Both the frequency shift and change in attenuation can be described as functions (g_1 and g_2) of the shear modulus:

$$\Delta f = g_1(\Delta m, \Delta G', \Delta G''),$$
(11)

$$\Delta \alpha = g_2(\Delta G', \Delta G'').$$
(12)

The shear modulus of the polymer will change due to the absorption of the analyte into the polymer. The polymer swells, its thickness increases and density

changes. When the storage modulus G' is decreased, the polymer softens. This viscoelastic loading contributes to the sensor response though a change in wave velocity [27].

2.3.2 Solubility Parameters

For a coating to be repeatable and stable, solubility between the polymer, plasticizer and solvent must be determined. A first method for determining solubility is using Hildebrand's solubility parameters [31]. The phrase "like dissolves like" is a general rule of thumb to determine solubility. Generally, a polymer will dissolve well within a solvent if the Hildebrand solubility parameters of each are very similar [31]. The Hildebrand solubility parameter (δ) is determined from the cohesive energy density of the solvent (c), derived from the heat of vaporization (ΔH). This parameter is the simplest solubility parameter to indicate solvency behavior [31].

$$\delta = \sqrt{c} = \left(\frac{\Delta H - RT}{V_m}\right)^{\frac{1}{2}} \tag{13}$$

In this equation, R is the universal gas constant, T is the temperature and V_m is the molar volume.

A more detailed determination of the solubility of polymers can be predicted using Hansen solubility parameters (HSP) [31]. The foundation of the HSP is a division of the Hildebrand solubility into three components from dispersion forces δ_d, dipole forces δ_p and hydrogen bonding δ_h. The Hansen solubility parameters relate to the total Hildebrand solubility by [31],

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad\qquad (14)$$

Using Hansen's solubility parameters, each individual component can be compared between materials. Materials with comparable solubility parameters will have a high affinity for one another.

Equation (15) was developed by Skaarup [31] using the partial solubility parameter components to calculate a solubility parameter "distance," RA, between two materials.

$$(RA)^2 = 4(\delta_{d2} - \delta_{d1})^2 + \left(\delta_{p2} - \delta_{p1}\right)^2 + (\delta_{h2} - \delta_{h1})^2 \qquad (15)$$

Once the distance RA is determined, this quantity must be compared to the experimentally determined radius of the solubility sphere, R_0 where $R_0 = 8.6$. For high affinity, the calculated radius, RA, must be less than R_0. The ratio between these two values, shown in (16), is known as the relative energy difference (RED) number.

$$RED = \frac{R_a}{R_0} \qquad\qquad (16)$$

The condition for solubility is $RED < 1$. A value equal or close to 1.0 is a boundary condition for solubility and values growing larger indicate a decrease in affinity between the two materials [32].

2.3.3   Glass Transition Temperature

Physical states such as solid, liquid, and gaseous are sufficient to describe the states of matter of many materials of low molecular weights. Their melting and boiling

points are the first-order transitions that define the change between these three states. Polymers with high molecular weight do not follow this same change of phase. At high temperatures, they decompose before their boiling points and will not vaporize into a gas. Instead, the transition that occurs at higher temperatures is a transition between rubbery and viscous. At lower temperatures, they do not crystallize like typical materials. The transition that polymers go through is called the glass-rubber transition, or simply the glass transition [33].

The glass transition temperature of a material, T_g, is the temperature at which the state of the polymer changes from rigid, hard, or glasslike to rubbery and more flexible. There is a relaxation of internal stress as the material transitions from the hard to soft state. At this temperature, there are abrupt changes in the physical properties of the material such as Young's and shear moduli, specific heat, coefficient of expansion, and dielectric constant [34]. Below the transition temperature, the thermal, long-range rotational and translational motion of the molecules in the material stops and the chains are no longer mobile causing the polymer to be glassy and rigid. The relation between the storage and loss modulus in this region is $G'' \ll G'$. A typical glass film occurs when $G' \cong 10^9$ Pa [35]. As temperature increases towards the glass transition temperature, the storage modulus, G', decreases rapidly while the loss modulus, G'', increases. The polymer starts softening during this change of shear modulus. Above the transition temperature, the polymer is soft and rubbery. A rubber film occurs when $G' \leq 10^7$ Pa and $G'' \leq G'$ [27], [36].

The glass transition temperature of different polymers varies due to molecular weight, chemical structure, addition of plasticizers, pressure, level of cross-linking and the distribution of amorphous and crystalline regions [33]. The viscosity found at this changing point is independent of the polymer's chemical structure, therefore the same for all polymers. Viscosity of the polymer is related to the volume between the polymer molecules. These glass transitions happen at the same fractional free volume for all materials [37].

For SH-SAW sensing, the coating must be at least partially rubbery to allow for good absorption of the analyte into the polymer coating. If the polymer used has a high glass transition temperature, the coating will be in a glassy state at room temperature where experiments are conducted. The glassy nature of the polymer will produce slow absorption rates of the analyte, which produce slow response times and low sensitivity. If the polymer has a very low glass transition temperature, the coating will be in a very rubbery state. This will allow for good sensitivity and fast absorption, but results in high acoustic-wave loss. There must be a middle ground between the two extremes. Using a polymer that has a glass transition temperature near experimental operating temperatures allows for this compromise. For polymers that have a high glass transition temperature, the addition of a plasticizer can be used to lower the glass transition temperature. This allows high glass transition temperature polymers that have a high affinity for BTEX absorption to be used in chemical sensing applications. The theory of plasticization to lower the glass transition temperature will be discussed next.

2.4   Plasticizer Theory

The addition of a plasticizer to a polymer material creates increased flexibility of a rigid polymer. The plasticizer interacts with the chains of the polymer to increase chain mobility and speed up the viscoelastic response. There are various theories that explain the plasticization mechanism [37].

2.4.1   Lubricity Theory

Many scientists contributed to the lubricity theory of plasticizers. According to this theory, the addition of a plasticizer reduces the intermolecular friction that occurs between the polymer molecules [37]. The polymer matrix is thought of as a lattice where the rigidity of the material is due to the internal friction between the polymer molecules. The lattice contains voids between the polymer molecules and when a sufficient amount of plasticizer is added to this matrix, the plasticizer molecules fill these voids. Cohesion forces between polymer molecules are reduced, allowing for movement and rotation. Planes are created that allow for easy glide of the polymer, thus increasing the mobility of the molecules resulting in an increased overall flexibility [37]. The plasticizer molecules act as a lubricant, thus the name of the theory.

2.4.2   Gel Theory

In the gel theory, the polymer matrix is thought of as a three dimensional honeycomb structure. The polymer molecules have loose attachments to one another along the chains. The rigidity of the polymer, according to this theory, is due to the

three dimensional structure resistance. Plasticizers can be added to reduce the attachment points that connect the polymer molecules to one another. Reducing the number of attachments decreases the areas of aggregation of polymer molecules and allows for the polymer to be deformed without breaking, thus increasing the overall flexibility [37].

2.4.3   Free Volume Theory

The free volume theory was developed years after the gel and lubricity theory. This theory explains how the addition of a plasticizer to a polymer lowers the glass transition temperature of that polymer. The viscosity of polymers at the glass-transition temperature was found to be independent of the polymer's chemical structure. This describes the viscosity as being related to the volume between molecules. It can be explained that the glass transition happens at a state where materials have the same fractional free volume [37].

The specific volume of a polymer decreases in a linear fashion with respect to the decrease in temperature. This linear dependence only occurs until the glass transition temperature. Below that temperature, the volume still decreases as temperature decreases, but at a much smaller rate [37]. If the linear curves above the glass transition temperature are extrapolated, all materials intersect at the same point, at absolute zero. At absolute zero, all molecular motion ceases. This volume represents the remaining space between molecules. The volume change between absolute zero and the transition temperature is constant for all polymers (0.0646 cm^3/g) [37].

Between the atoms and molecules in the polymer matrix there is only free

volume. Free volume is determined as the difference in volume at a specific

temperature and the volume of that material at absolute zero.

$$V_f = V_t - V_0 \qquad\qquad (17)$$

When there is an addition of a plasticizer, this free volume increases. The plasticizer

molecules are situated between polymer molecules which expands the polymer matrix,

adding more free volume to the final material. A larger free volume within a material

corresponds to increased flexibility and movement of macromolecules. For chemical

sensing, a larger free volume increases the ability of the polymer to absorb analytes.

2.4.4 Effect of Plasticization on Sensing Parameters

Each of these theories of plasticization can be used to describe the condition of a

plasticized polymer. For chemical sensing applications, it is important to look at the

sensing parameters and the effects due to the addition of a plasticizer. All of the

theories describe the same type of behavior, increased flexibility. When there is

increased flexibility, there is an increase in sensitivity. If a polymer is hard and rigid, it

will not absorb any external molecules. In the case of a plasticized polymer, there is

increased movement or increased free volume within the polymer. This allows for an

analyte to be absorbed into the polymer at a faster rate. With higher mobility and larger

free volume, the number of analyte molecules that can be absorbed into the coating

increases. The increased number of absorbed molecules creates a larger mass loading

on the sensor which will result in a larger frequency shift. This increased frequency shift

results in the increased sensitivity of the device. Increased flexibility also increases the rate in which analyte molecules are absorbed, therefore shortening the time response of the device to the measurand.

The addition of a plasticizer to increase flexibility and therefore sensitivity comes with a cost. The increased plasticity also increases the loss of energy from the SH-SAW, as the polymer is more rubbery. When the coating on the SH-SAW device is very rigid, the loss is low. The coating moves synchronously with the substrate. The energy is confined and remains in the device. As you increase flexibility to allow for greater absorption of the analyte, the rubbery coating causes an increase in the loss. There has to be a compromise between glassy and rubbery to allow for a sensitive coating with acceptable loss.

2.5   Stability in Water

The goal of this research is to create a new coating suitable for the detection of BTEX compounds in the liquid phase that has high sensitivity and is stable long term. The desired coating would be capable of making many repeatable measurements over a relatively long period of time. For the above requirement to be plausible, the coating must be stable over time. For plasticized polymers, plasticizer leaching rates have been previously studied [38]. It was found that many commercially available plasticizers, such as the commonly used dioctyl phthalate (DOP or DEHP), have a leaching rate of 0.8% per week [38] into a surrounding liquid environment [38]. The leaching rate of the plasticizer

into the surrounding liquid depends heavily on the chemical structure and polarities of the liquid and plasticizer.

Leaching rate into the aqueous phase is lower when there is a high hydrophobicity of the plasticizer molecule [38]. The higher leaching rate of DOP is caused by the saturated ring system and short hydrocarbon chains. The leaching rate of DINCH is undetectable [38] and is due to the higher hydrophobicity of the molecular structure. DINCH still has a middle group that is polar enough to be miscible in the polymer, but it has long nonyl chains that are extremely hydrophobic. The difference in their leaching rates also can be explained by their difference in solubility in water [38].

2.6   Choice of Polymer and Plasticizer

The results of [36], [18], and [39] show increased sensitivity to aromatic hydrocarbons in water using a QCM and SH-SAW sensor when coated with polymer-plasticizer films. In [36], the combination of DOP-PS yielded the greatest sensitivity to benzene. The high sensitivity suggests polystyrene as an ideal polymer for aromatic hydrocarbon sensing applications when plasticized. The chemical structure of polystyrene supports the affinity to aromatic hydrocarbons. Polystyrene is a long hydrocarbon chain containing benzene rings (phenyl groups). Benzene, toluene and ethylbenzene are often used as solvents with polystyrene [40] because of their high affinity for this polymer. Polystyrene has a high glass transition temperature calculated to be 99-108° C [40] and must be plasticized to lower the glass transition temperature for use in chemical sensing.

Plasticizers with an extremely low or non-existent leaching rate are desired for long term applications in liquid-phase operation. The plasticizer DINCH was chosen due to an undetectable leaching rate in water [38]. The solvent chosen was tetrahydrofuran (THF). THF is a known good solvent for polystyrene [40].

Solubility of all materials with one another was further determined using the results from equations (15) and (16) and the Hansen solubility parameters in Table 1. The results corresponding to each combination of polymer, plasticizer and solvent are shown in Table 2.

	δ_d	δ_p	δ_h
THF	16.8	5.7	8
DINCH	15.4	6.18	5.25
Polystyrene	18.6	6.0	4.5
Benzene	18.4	0	2.0
Toluene	18.0	1.4	2.0
Ethylbenzene	17.8	0.6	1.4
o-Xylene	17.6	1.0	3.1

Table 1: Hansen's solubility parameters for materials used (solvent, plasticizer, polymer, and analytes) [41] [42]

Material 1	Material 2	$\Delta\partial_d$	$\Delta\partial_p$	$\Delta\partial_h$	RA	RED
THF	DINCH	1.4	-0.48	2.75	3.953846	0.45975
THF	Polystyrene	1.8	-1.2	-5.1	6.356886	0.739173
DINCH	Polystyrene	3.2	-1.68	-2.35	7.021745	0.816482
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
o-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
o-Xylene	DINCH	2.2	-5.18	-2.15	7.128457	0.82889

Table 2: RA positions and RED numbers calculated from (15) and (16) using values in Talble 1 for each combination of polymer, plasticizer, solvent and analyte

The above analysis shows solubility between all materials used. The BTEX compounds with DINCH show close to and borderline solubility. This is not of concern because the percentage of plasticizer in the blend is under 30%, and the main solubility concern for the BTEX compounds is with the polymer. Polystyrene shows good solubility with all BTEX compounds.

3   Experimental Procedure

3.1   Introduction to Methods

A brief summary of the experimental procedure steps follows below. First, the

desired coating for the chemical sensor is prepared as a polymer-plasticizer blend in an

appropriate solvent. The coating is then deposited by means of a spin coater onto an

SH-SAW device which was previously cleaned of any organic contaminants. The

thickness of the coating is determined by using either a profilometer or an ellipsometer.

The device goes through proper preparation, described later in this chapter, and is

inserted into the flow cell specifically designed for this application. The sensor is

exposed to a reference sample of deionized water or an analyte solution by means of a

pump and three way valve. A network analyzer is used to monitor the device loss,

frequency and attenuation at a constant phase when exposed to the analyte solution

and reference sample. In this chapter, this procedure along with the materials and

equipment used will be discussed in further detail.

3.2   Equipment and Materials

3.2.1   Sensing Device

The device used for data collection is an SH-SAW device specially designed by the

Marquette University Microsensor Laboratory. The substrate used for the device is

lithium tantalate (LiTaO$_3$). The IDT fingers are made of metalized gold on a thin adhesion

layer of titanium or chromium and are patterned in a two-ten finger pair manner [43],

[44]. The delay line is also coated with gold/titanium (or chromium) layer which is grounded to prevent any electrical interaction when in the aqueous environment. The frequency used for operation is tracked during measurements and is typically around 102 MHz. Choice of the operating frequency depends on the linearity of the phase and must be a frequency within the 3-dB passband.

Figure 5: DINCH-PS coated SH-SAW device [Picture taken at Microsensor Research Laboratory, Marquette University, 2016]

3.2.2   Chemical Materials

The delay lines and IDTs are coated with a thin polymer-plasticizer film. The contact pads are protected during the coating procedure. The construction of the flow cell design [26] allows for only the IDTs and delay lines to be exposed to the aqueous environment. Details of the device preparation and flow cell design will be explained in sections to follow.

Various polymer-plasticizer blends were studied in this thesis. All blends use the same polymer base: polystyrene (PS). Polystyrene is a commercially available polymer that was purchased from Sigma Aldrich. It has a high glass transition temperature, calculated between 99-108°C [40], and therefore needs the addition of a plasticizer to lower its glass transition temperature. Two different plasticizer additives were investigated: dioctyl phthalate (DOP) [45] and 1,2-Cyclohexane dicarboxylic acid diisononyl ester (DINCH) [46]. Both of these plasticizers are commercially available. Dioctyl phthalate was purchased from Sigma Aldrich and DINCH was obtained from the BASF Corporation. The DOP-PS mixture was dissolved in chloroform and the DINCH-PS mixture was dissolved in tetrahydrofuran (THF). Both of these solvents were purchased from Sigma Aldrich.

All four BTEX compounds, benzene, toluene, ethylbenzene and xylenes, were investigated in this study. All were purchased from Sigma Aldrich. The analyte solutions were made in deionized degassed water made in-house in the Microsensors Research Laboratory at Marquette University.

3.2.3 Spin Coater

The spin coater used for depositing the polymer-plasticizer blend is a Specialty Coating Systems (SCS) Model P6024. The device is centered on the chuck of the spin coater and a vacuum is applied to hold the device in place. The spin coater allows for the user to create specific "recipes" that are individualized for the user's specific coating solution. Ramp up times, spin speeds, spin times, ramp down times are the main

variables that are controlled. Depending on the properties of the coating solution (viscosity and solvent evaporation rate) and the spin coater settings (spin speed, duration time, and acceleration), various thicknesses and uniformity of the coating can be achieved. Having control over the specific settings allows the user to preset variables for a fast, easy, reproducible deposition of the final coating. For this research, thin, uniform films are required for repeatable, reproducible, and reliable results.

3.2.4   Thickness Characterization Devices

There are two methods available in the laboratory for measuring the thickness of a film. One is a contact method, the other is a non-contact method. The contact method is performed by the profilometer. The profilometer used is an Alpha Step IQ profilometer. A microscopic stylus tip is dragged across the surface to measure the step height profile of the coating. Because this is a contact method, the actual device is not used due to potential damage from the stylus. Instead, a small portion of a glass slide is used as the substrate and undergoes the exact same deposition procedure at the same time to replicate the coating on the actual device. The profilometer allows the user to specify settings (such as scan length, scan speed, and sampling rate) to accurately measure thickness of the specific sample created. The stylus force can also be adjusted for specific coatings and will depend on the coating rigidity. Softer, more rubbery polymers require an extremely low stylus force to be used so that the stylus tip will glide over the surface smoothly without penetration. Penetration not only scratches the polymer, it gives an inaccurate measurement of the thickness.

The second method is the non-contact method. This is performed by the ellipsometer. The ellipsometer used is a product of the Gaertner Scientific Corporation. It uses both a green (543.5 nm) and red (632.8 nm) laser. The laser is incident to the coating surface at an oblique angle. The laser partially transmits through the coating surface, is reflected from the substrate, and transmits back through the coating surface to a receiver, which also receives the beam reflected from the top surface of the coating. The software uses information gathered about both reflected beams to determine both the index of refraction and the thickness of the coating film. Care must be taken when measuring coatings that have wavy surfaces which causes problems with the reflections giving inaccurate, or indeterminable results. A scan made by the profilometer determines if the surface profile is suitable for ellipsometer measurements.

3.2.5   Flow Cell

The device is housed in a flow cell designed for the Marquette University Microsensor Laboratory [26]. The flow cell is comprised of three pieces shown in Figure 1. Two pieces of brass make up the shell (base and middle piece) to hold the device in place, ground the delay line and connect the input and output transducers of each delay line to the network analyzer through coaxial cables. The third piece (top) is the Plexiglas cover that has channels to allow liquid enter and exit the chamber as it flows over the device. A rubber gasket is used to isolate the aqueous environment from the contacts on the device. Only the IDTs and delay lines are in this channel exposed to the liquid.

Figure 6: Individual parts of the flow cell used to house the SH-SAW sensor: brass middle piece with connecting pins (left), shell base to hold the device in place (center), and Plexiglas cover with gasket and inlet/outlet tubes to channel the solution over the device (right). [Picture taken at Microsensor Research Laboratory, Marquette University, 2016]

3.2.6 Peristaltic Pump

The flow cell is connected to a pump that forces the liquid solution across the sensor. The pump is manufactured by IDEX Corporation. It is an Ismatec pump that allows the user to set the speed of the liquid flow. The analyte solutions are kept in closed containers that allow for a small tube to be inserted and extract the sample. This prevents the analytes of interest from evaporating into the air, which would cause a decrease of the concentration over the time of the experiment yielding inaccurate results. The pump pulls the liquid from the analyte or reference sample through the flow cell and into a waste container. A three-way valve is used to direct flow of the reference sample or the analyte sample to the flow cell. The three-way valve allows the

user to continually run the experiment without stopping the pump to change solutions.

Stopping the pump and changing solutions causes spikes in the response due to a

pressure change. The three-way valve eliminates this problem. Measurement continues

smoothly while changing solutions quickly to produce a step change in concentration.

3.2.7   Network Analyzer

A network analyzer is used to send multiple frequencies through the SH-SAW

device and collect the output data. The network analyzer used in these experiments is

an Agilent E5061B. The network analyzer is connected to an Agilent 34980A

multifunction switch/measure unit. This switches the signal sent to the computer

between the two SH-SAW delay lines. Device loss, frequency and amplitude are

measured over the experiment for both delay lines to characterize each in the presence

of the reference sample and the analyte sample.

3.2.8   Experimental Set Up

The diagram of the experimental set-up can be seen in Figure 5. The analyte

solution or reference solution passes through the three-way valve into the flow cell

chamber and is drawn into the waste container by the peristaltic pump. The flow rate is

set to 7 $\mu L/second$ for all experiments. The flow rate needs to be consistent through all

measurements so response times can be compared, if desired. The flow cell housing

connects the contact pads of the device to the coaxial cables that send and receive

signal from the network analyzer. A switching unit switches between both lines on the

device. Data is collected every 12 seconds (or lower) through the Agilent software on

the connected computer.

Figure 7: Experimental schematic used to measure two-port insertion loss and frequency response for the plasticizer-polymer coated SH-SAW sensor exposed to reference/analyte solution

3.3   Preparation Procedures

3.3.1   Device Preparation

There is an initial preparation step that occurs for all new SH-SAW devices to

produce optimal device performance. The goal of the preparation is to reduce acoustic

wave reflections from the substrate ends behind the transducers and also reduce wave

components from wave propagation through the bulk of the substrate. A properly

prepared device will have low passband ripple and low acoustic loss and will provide experimental reproducibility. Preparation steps include:

1. Characterize the unprepared device by measuring the spectrum using the network analyzer and save for reference. The spectrum can be saved to the VNA memory and recalled for direct comparison.

2. Use sand paper (type #40) to bevel the short side of the device substrate at approximately a 45° angle. Sanding at an angle allows for any reflected wave to be directed away from the IDT.

3. Periodically measure the spectrum and compare to initial spectrum to check if the passband ripple is smoothed out and reduced.

4. Once the ripple has been reduced sufficiently, sand a groove behind each of the IDTs and contact pads.

5. Place insulating tape (black electrical tape) on the bottom side of the device. This absorbs energy from the incident bulk wave.

   Measure the spectrum once again for device baseline records.

3.3.2   Coating Preparation

The same procedure was followed for both DOP-PS and DINCH-PS coatings. Weight percent of the plasticizer to polymer varies as well as the weight percentage of polymer-plasticizer in the solvent. Various plasticizer percentages give different response results. The percentage in the solvent affects the viscosity of the solution. This

viscosity plays an important role for the resulting coating thickness. The weight/weight

definition used to calculate plasticizer percentage is given by,

$$wt\% = \frac{mass\ of\ plasticizer\ (g)}{total\ mass\ of\ plasticizer\ and\ polymer\ (g)} x100. \qquad (18)$$

And the percentage of the polymer-plasticizer blend in the solvent is given by,

$$wt\% = \frac{mass\ of\ polymer\ and\ plasticizer\ (g)}{total\ mass\ of\ solution\ (g)} x100. \qquad (19)$$

The coating solutions were prepared by the following steps:

1. Tare a clean vial with a stir bar on a microbalance.

2. Add desired mass of polymer.

3. Calculate desired amount of plasticizer to achieve correct w/w percentage.

4. Add desired amount of plasticizer.

5. Calculate the desired amount of solvent to achieve correct w/w percentage of

   polymer-plasticizer in the solution.

6. Add desired amount of solvent.

7. Immediately close the vial and seal with Teflon tape to prevent evaporation.

8. Place on magnetic stir plate and stir at ~ 600 rpm overnight.

9. The following day, sonicate the solution for four hours straight. Solution will heat

   up.

10. Allow the solution to cool down and allow for any bubbles to migrate to the top

    of the vial before coating.

3.3.3 Device Cleaning Procedure

Before the devices can be coated, they need to be properly cleaned of any old polymer residue, tape residue, and any other organic contaminants. Having such contaminants on the surface of the device leads to improper adhesion of the coating and can cause pinholes and delamination. This creates irreproducible coatings. Cleaning steps include:

1. Wash the device with four organic solvents in this order: trichloroethylene, chloroform, acetone, and n-propanol. This is a general degreasing procedure that removes most oils, finger grease and organic deposits. The steps taken for washing in the solvents include:

    1.1. Place device in solvent jar.

    1.2. Place in sonicator for 5 minutes.

    1.3. Remove device from jar and rinse with DI water for 15 seconds (for first three solvents, skip for n-propanol).

    1.4. Dry device with nitrogen.

    1.5. Repeat for next solvent.

2. A harsher chemical cleaning is used to remove residual organic and ionic contamination from the surface. Trace organics, chemically adsorbed monolayers of organics, and physically adsorbed monolayers of adventitious organics (layers that are not covalently bonded to the surface) are removed. Steps include:

2.1. Mix a solution of 5:1:1 H_2O : NH_4OH : H_2O_2 and heat to approximately 65-70 °C. Start with the water, slowly add the ammonium hydroxide, then slowly add the hydrogen peroxide. Heat a similar sized jar of water on the same hot plate for temperature verification. If the temperature is too high, damage to the IDTs can occur when sudden temperature change occurs from removal of the device.

2.2. Place the device in the heated mixture for 5 minutes.

2.3. Remove the device and rinse with DI water for 30 seconds. Check to make sure device is wetting properly (surface should be hydrophilic). If not fully wetting, place back into solution for additional time.

2.4. Dry with nitrogen.

3. The final cleaning step involves UV cleaning. This removes any last contaminants by breaking their bonds from the surface of the device. Place the device approximately 1 cm from the UV lamp. Let the device sit underneath the lamp for one hour. The temperature of the device will remain in a safe range. After one hour, remove the device and coat immediately.

Note: Make sure to follow proper safety procedures for all cleaning steps. Wear proper attire and protect stray UV rays from leaving the cleaning chamber.

3.3.4 Coating a Device

The device is coated with the selected plasticizer-polymer blend to act as a guiding layer for the surface wave as well as the chemically selective layer that absorbs

the analyte. Proper procedure for coating the device must be followed to ensure reproducible, uniform coatings. The steps below were followed for coating all devices.

1. Mask the contact pads (or delay line if coating a reference line) with Kapton tape to prevent unwanted area from being coated.

2. Blow the surface off one last time with nitrogen to remove any dust or small particles that may be introduced from the air.

3. Center the device on the chuck of the spin coater.

4. Adjust the spin coater settings for the specific coating to be deposited.

5. Cut approximately 6 mm off of the end of a plastic micropipette tip (100 – 1000 µL). This should create a larger opening at the end of the tip (2-3 mm in diameter). This allows for faster deposition of the coating solution, which is very important for more volatile solvents.

6. Dispense 350 µL over the entire area of the device (Amount of liquid dispensed depends on viscosity of the solution. There should be just enough solution to fully cover the device.)

7. Immediately close the lid of the spin coater and press start. There should be minimal time between deposition and the start of the spin coater to prevent as little solvent as possible from evaporating before the spin coater starts.

8. Remove device from chuck.

9. Place in tin foil boat, cover and place in the oven.

10. Bake for 60 minutes at 60°C to remove excess solvent.

11. Once baked, remove Kapton tape to expose the contact pads and add black

absorbing tape on the back of the device. Note: make sure black tape does not

extend past the edges of the device and that there are no air bubbles or debris

between the tape and the device as this could cause problems with the device

fitting in the flow cell properly.

Carefully add conductive silver paint onto the contact pads to ensure good

electrical contact between the device and the flow cell. Note that this step is not

necessary if the IDT contact layers are not scratched.

3.3.5 Preparing Analyte solution

Analyte solutions must be prepared consistently to ensure accuracy of the

analyte concentration. Even though concentrations are verified after every

measurement, it is important to prepare the same concentration sample for long term

stability measurements. The signal noise is more noticeable when measuring smaller

concentrations. When responses are normalized, the noticeable noise at lower

concentrations is amplified. It is best to prepare a stock solution and dilute down to the

desired concentration, though a solution may be directly prepared. Preparing a stock

solution and diluting down reduces the relative error in sample preparation.

1. Calculate desired volume of the analyte, based on the total volume of degassed,

    deionized water used for the solution, to produce the desired analyte

    concentration. A stock solution of higher concentration was initially made (10-

    30ppm).

2. Measure exact volume of degassed, deionized water using a flask and a

    millipipette into a jar with a magnetic stir bar. There should be minimal headspace

    to prevent analyte evaporation.

    2.1 Degassed water is generated by boiling deionized water for at least 3

        hours and immediately sealing container after the water has cooled down.

3. Add desired volume of analyte and immediately seal the jar.

4. Place on stir plate and stir overnight at ~ 600 rpm.

5. The following day, dilute the stock solution to desired concentration for

    experimentation.

6. Allow solution to stir for at least one and a half hours before using in an

    experiment.

Note: Solutions are made within 2 days of experimentation. Over time, analyte

evaporates, contamination can occur, and air can diffuse back into the water causing it

to no longer be degassed and may create bubbles during the experiment.

3.4   Experimental Procedures

3.4.1   Thickness Characterization

Coating thickness was verified for every device. The coating was replicated on a

piece of a glass slide allowing for thickness characterization using the profilometer. The

profilometer scans across the surface of the glass and plasticizer-polymer coating to

measure the profile and allows for a differential calculation to be made to determine

the thickness. The maximum scan length of the profilometer is one centimeter. Because of this limitation, a portion of the coating is scratched off using a razor blade to provide the end of the scan with a glass surface. Having the profile start and end on glass allows for accurate leveling of the scan.

The glass slide is placed on the tray, moved into position and raised up to the stylus. Proper settings are used for stylus force, scan length, scan speed and sampling rate. Once the scan is completed, the surface profile data is leveled and filtered for any excess noise from outside sources such as vibrations due to footsteps or busses passing by the building. A step height differential is made to calculate the thickness of the coating.

3.4.2   Device Response

When all preparation steps are completed, the device is secured in the brass bottom of the flow cell. The cover is carefully placed on top and secured. It is important to make sure the gasket is properly in place before securing the cover. Once the gasket comes in contact with the coating, it should not be removed. Removing the cover and gasket also removes part of the polymer.

The coaxial cables connect the device so that the data can be sent from the network analyzer to the corresponding software on the PC. The inlet side of the flow cell, reference sample and analyte solution are connected to the three-way valve. The outlet side of the flow cell is connected to the pump. The pump is turned on and set to 7 μL/second. The sensor is exposed to the analyte and reference samples long enough to

allow for steady state equilibrium of analyte absorption and return to baseline from analyte desorption to occur. Device loss, frequency and amplitude are monitored by the Agilent software on the connected computer. Data processing will be discussed in section 3.4.4.

3.4.3   Concentration Confirmation

Confirmation of analyte solution concentration was determined by the GC-PID (Gas Chromatography – Photoionization Detector) (Defiant FROG-4000). The GC-PID uses a micro preconcentrator, micro gas chromatographic column and a photoionization detector to determine the concentration of volatile organic compounds in water [47]. The FROG was frequently calibrated using BTEX standards to ensure accurate determination of the concentration. The error in concentration is within 10% up to 1ppm for the BTEX analytes. Above this range, the calibration becomes non-linear. Solutions with concentrations larger than 1ppm were first diluted before measured with the FROG. Dilution adds a small error due to multiple volume measurements rather than one, but the error from dilution is smaller than that of the GC-PID operating outside of the calibration range.

3.4.4   Data Processing

Once data is collected, a linear baseline correction due to sensor drift is made. Adequate time is allotted before data collection to ensure baseline drift is in the linear range. Once frequency shift data is corrected for the baseline drift, the data can be

normalized using the concentration of the analyte determined by the GC-PID for

comparison using:

$$f_n = f_0 \left(\frac{C_n}{C_0}\right)$$
(20)

where f_n is the normalized frequency, f_0 is the raw frequency, C_0 is the concentration

determined by the GC PID, and C_n is the normalizing concentration. Frequency

responses from different experimental days can then be compared to determine

repeatability. Note that normalization will also affect the noise in the sensor response

data. As a result, noise calculations and detection limits are determined from the

original, non-normalized data. The frequency response data can be fit using a single

exponential fit (for one analyte) [10]:

$$y(t) = y_0 \left(1 - e^{-\frac{t}{\tau}}\right)$$
(21)

where $y(t)$ is the frequency at time t , y_0 is the total frequency shift and τ is the time

constant. The time constant is defined as the time it takes the sensor to respond the

introduction of the analyte, represented as a step input, to reach $\left(1 - \frac{1}{e}\right) \approx 63.2\%$ of

the final, asymptotic value for the sensor [11] and should not be confused with response

time. The extracted features (time constant and frequency shift) are the two parameters

that help to characterize a sensor coating. The frequency shift is used to determine the

sensitivity S, which is defined as [10],

$$S = \frac{\Delta f}{C_0}.$$
(22)

High sensitivity is an important parameter when sensing low concentrations. The limit of detection (LOD) determines the lowest concentration a sensor can detect. The LOD is determined based on the sensitivity and the noise level of a sensor as [9]

$$LOD = \frac{3 * RMS\ Noise}{Sensitivity} \qquad (23)$$

where the RMS noise is calculated using the standard deviation of the baseline of the frequency response. Having a coating that produces low noise and high sensitivity will result in very low detection limits.

4   Results and Discussion

4.1   Introduction

In this work, the use of DINCH as a plasticizer for polystyrene to create a SH-SAW coating sensitive to BTEX compounds was investigated in detail. Initial stability of the DOP-PS coating from [36] was investigated (best plasticizer-polymer sensor coating was found to be a 1.1μm-thick 23.0% DOP-PS). The percentage of DINCH plasticizer/polymer and coating thickness were varied and sensitivity, response time, noise level, limit of detection, and stability were studied. Previous work with other sensor coatings has been done in larger concentration ranges [22], [23] [36]. The goal of this work was to create a highly sensitive coating capable of measuring concentrations in the parts per billion (ppb) range. The concentrations of analyte samples prepared in this work never exceeded 5 parts per million (ppm).

The device was initially exposed to water to allow the polymer to absorb the liquid and swell. This swelling increases the thickness of the device and changes the viscoelastic properties of the coating. Adequate time was allowed for the polymer to fully absorb any water and come to equilibrium. Temperature changes also affect the sensor frequency response. Changes due to heating/cooling or other perturbations in the room will affect the ambient temperature, but at a very slow rate. This does not affect sensor responses for analytes with fast response times. For analytes with long response times, the ambient temperature changes should be kept to a minimum. A thermistor attached to the bottom of the flow cell is used in the experiment to track the

temperature. Temperature can be tracked to ensure that data collected and analyzed were taken during stable ambient conditions. Rapid changes in temperature, such as a temperature differential between the reference sample and analyte solution, will cause an immediate effect on the response. To eliminate this effect, sufficient time was allowed for all solutions and materials to come to the same equilibrium temperature before experimentation. Even after polymer swelling has completed and temperature has stabilized, there will still be some linear drift that affects the device loss, frequency and amplitude that are monitored by the network analyzer. This drift was corrected for during data analysis.

The coated SH-SAW device was exposed to various analyte solutions. A network analyzer was used to measure and record changes in frequency, phase and loss that occurred due to sensor perturbation from the exposure to the analyte. The initial operating frequency was chosen to track the change in frequency at a constant phase. This frequency change is used to determine the sensitivity of the device. The change in frequency is plotted as a function of time for various analyte concentrations. The frequency response is corrected for linear baseline drift and the data is normalized to the concentration of the analyte. This allows for a visual determination of repeatability of the sensor on various experimental days. The steady state frequency shift can be extracted from a plot of the change in frequency of the raw data over time. A single exponential fit is used to model the data and extract the steady state frequency shift as well as the time constant for the response. The extracted frequency response features are plotted as a function of the analyte concentration to create a calibration curve for

the specific sensor coating. A separate calibration curve is made for each BTEX analyte that is tested. The slope of the calibration curve represents the sensitivity of the coating to the analyte. If multiple analytes are tested, sensitivity comparisons allow for partial selectivity of the coating to be determined. Noise levels of the baselines are calculated and detection limits of each coated sensor for different analytes are determined. All outliers are filtered before sensitivity and detection limit calculations.

4.2   Initial stability investigation of previously studied plasticizer-polymer sensor coating

The previous investigation of a plasticizer polymer sensor coating from [36] found a 1.1μm-thick 23.0% DOP-PS to be the best coating for sensitivity to benzene. Measurements of approximately 1ppm were used to test the reproducibility and stability of a 1.21μm-thick 23.4% DOP-PS on four different experimental days over the span of 47 days, shown in Figure 8. It should be noted that concentration of benzene was not verified by the GC-PID. Samples were prepared to be 1ppm benzene.

Figure 8: Frequency response to benzene (main) and tracked device insertion loss at the operating frequency (insert) of the 1.2μm-thick 23.4% DOP-PS coated SH-SAW sensor for 1ppm benzene for a period of 47 days [Note: Concentration was not measured by the GC-PID].

The insert in Figure 8 shows that after about 10 days, the loss increased to the 35 dB experimental threshold. The measurement data from day 47 shows a large increase in noise which is expected due to the high insertion loss. Frequency shift due to 1ppm of benzene seems to be repeatable with a sensitivity around 700 Hz/ppm. This is an estimated sensitivity due to the concentrations of benzene not being measured by the GC-PID. The 1.1μm-thick 23.0% DOP-PS sensor coating is very sensitive to benzene, but is not stable for a long period of time. It is necessary to investigate a plasticizer-polymer sensor coating that can be made stable over a period of at least three months.

4.3   Effects of plasticizer percentage in the DINCH-PS blend

Polystyrene was the chosen polymer for BTEX detection. The work from [36]

shows polystyrene as a highly sensitive sensor coating with the addition of a plasticizer.

DINCH was chosen as the plasticizer to be added due to the low leaching rate in water. It

was the hope that DINCH-PS blends would be more stable than the DOP-PS blend. Table

2 shows the solubility of polystyrene with DINCH, THF and all BTEX compounds.

Polystyrene was determined to be soluble with all of these materials. All BTEX

compounds were investigated, but benzene was the focus of this project because of its

many hazards. Polystyrene has a high glass transition temperature and was plasticized

to lower the glass transition temperature to correspond with experimental operating

temperatures. DINCH was the plasticizer used due to its undetectable leaching rate in

water. It was predicted to be a suitable plasticizer for long term measurements in an

aqueous environment. The percentage of plasticizer added to the polymer determines

the final glass transition temperature of the plasticized polymer. Higher plasticizer

concentration corresponds to a lower glass transition temperature. Various percentages

of DINCH were investigated to determine an optimal plasticizer-polymer blend. Also,

different thicknesses of the coating were investigated. The optimization of thickness and

plasticizer percentage will allow for the most sensitive stable coating.

4.3.1   First blend (20.9% DINCH-PS)

Initially, a plasticizer percentage of around 20% was desired based on plasticizer

percentages in [36] and [38]. The actual concentration produced was 20.9 % DINCH-PS.

The obtained coating thickness was 0.8µm, which results in an initial insertion loss of -

19.8 dB. The low initial device insertion loss suggests the coating is near the glassy

regime and could be made thicker or more rubbery. Figure 9 shows the overlaid

normalized frequency responses of repeated measurements over 61 days. The

frequency response was normalized to 2 ppm benzene using the concentration

measured by the GC-PID for each experiment and s 30% weighted fit was used to

smooth the noise from the data. Concentrations of benzene ranged from 990 ppb to 2.5

ppm. Samples were diluted for concentration verification by the GC-PID due to the

calibration range extending to 1 ppm. There is a spread of about 50 Hz for the

equilibrium frequency. This can be due to the 10% error in concentration measured by

the GC-PID which affects the normalization. Though the ambient temperature and

sample temperatures should be stable, small changes in temperature are more

noticeable for a sensor with low sensitivity and may contribute to some of the sensor

response spread. Low sensitivity is shown in the next section.

Figure 9: Overlaid frequency responses of a 0.8μm-thick 20.9% DINCH-PS coated SH-SAW sensor normalized to 2 ppm benzene with a 30% weighted fit to smooth the noise. Experiments were conducted over a period of 2 months

4.3.1.1 Sensitivity

The frequency shift was extracted from the raw data and was plotted as a

function of the benzene concentration. The slope of this curve represents the sensitivity

of the sensor to benzene.

Figure 10: Frequency shift as a function of benzene concentration with a linear fit to extract sensitivity for a 0.8µm-thick 20.9% DINCH-PS coated SH-SAW sensor

The sensitivity for the 0.8µm-thick 20.9 % DINCH-PS coating to benzene was

determined from the slope of Figure 10 as 0.0632 Hz/ppb. Taking the measured noise

into account (3.6 Hz), this sensitivity to benzene correlates to a limit of detection (LOD)

of 170 ppb. The goal of this project is to find a sensitive coating that pushes the limit of detection below 100 ppb. This coating shows the feasibility of DINCH-PS as a sensor coating for benzene, but adjustments must be made to increase the sensitivity. This may be achieved by one of two ways: increasing coating thickness and/or increasing plasticizer percentage. Thicker coatings allow for a larger number of analyte molecules to be absorbed into the coating, causing a larger change in mass which increases the freq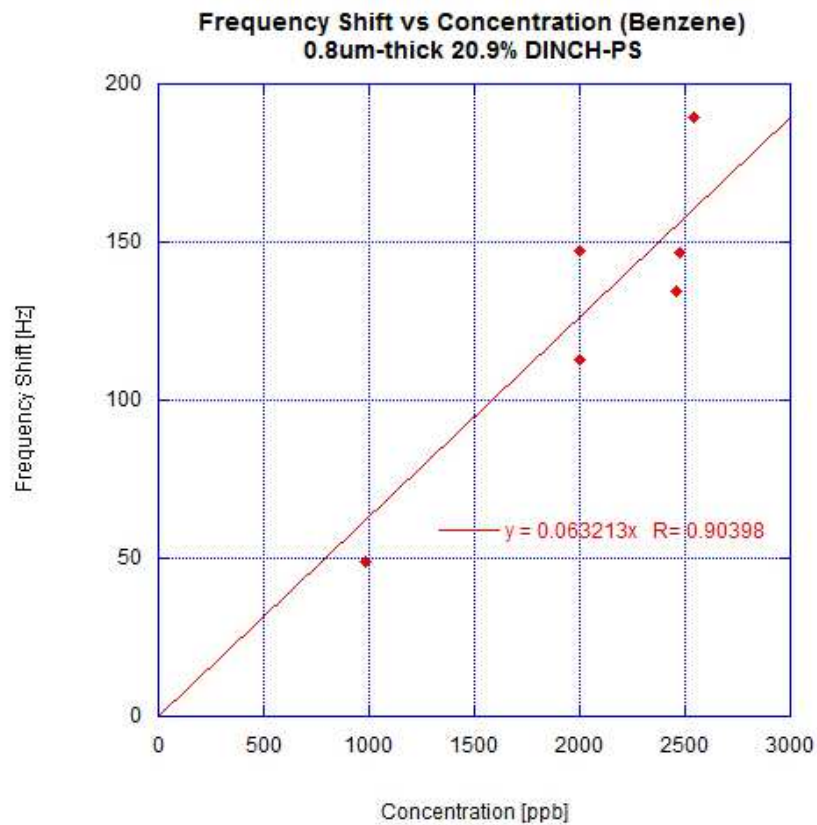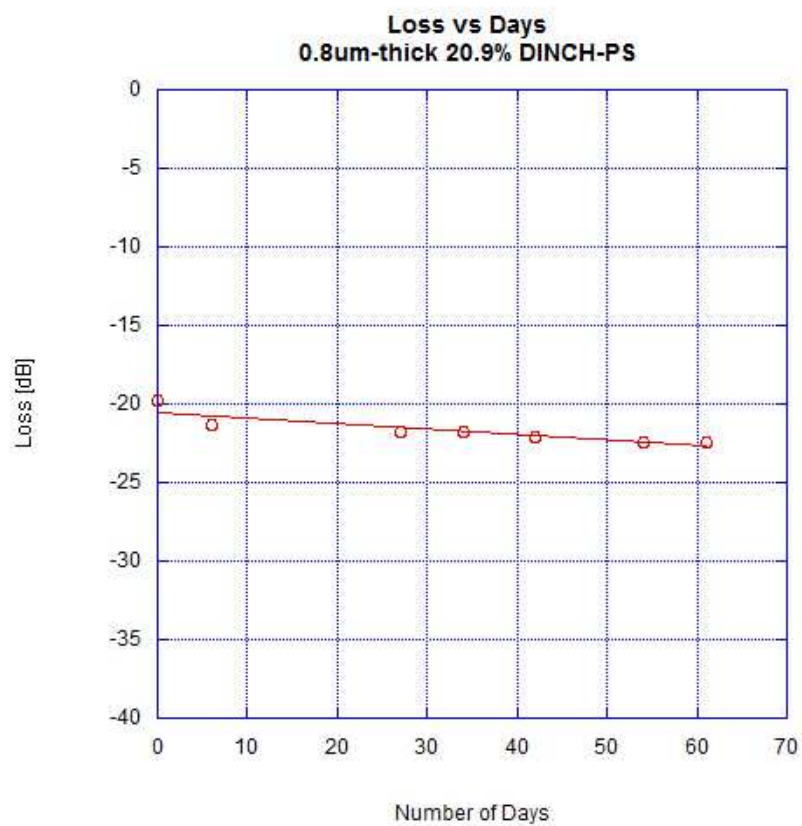uency shift response and thus, the sensitivity. Higher plasticizer percentages should soften the polymer resulting in a more rubbery polymer and increase the free volume further, again allowing for more analyte molecules to be absorbed.

4.3.1.2 Stability

Though the 20.9% DINCH-PS coating did not have high enough sensitivity, it did show stability over the 61 days of experimentation. The loss at the operating frequency (i.e. device spectrum) was tracked at the beginning of each measurement. The tracked insertion loss of this device is shown in Figure 11. As seen from the figure, the loss increased by about 3 dB over the course of two months. With the low initial insertion loss and the slow increase in loss, the device was determined to be very stable. It is believed that the device's stability is related to the glassy (or nearly glassy) nature of the polymer. The observed small loss may be due to a combination of the thin coating and physical state of the polymer. If the state of the polymer is more rigid or glassy, the polymer is expected to undergo little or no swelling on analyte absorption and thus show better long-term stability.

Figure 11: Device insertion loss at the operating frequency for the 0.8µm-thick 20.9% DINCH-PS SH-SAW sensor coating tracked for a period of 2 months.

4.3.2 Second blend (26.2% DINCH-PS)

Due to the low sensitivity of the low percentage of plasticizer (i.e. 20.9%), a sensor coating with a higher plasticizer percentage of 26.2 % DINCH-PS was produced and investigated. The coating thickness was slightly increased to 1.0μm. The resulting device sensitivity to benzene was found to be 0.355 Hz/ppb. The measured noise was low (5.2 Hz) and a very good detection limit of 45 ppb was determined. The initial insertion loss was -24.8 dB suggesting a coating that has undergone glass transition and is slightly rubbery. An insertion loss around 25 dB is ideal. It will allow for a 10 dB of loss increase before the coated devices becomes inoperable due to higher signal noise; this value of the insertion loss is also high enough to indicate that the coating is not glassy, and that the thickness of the coating is near the maximum acceptable value.

After preconditioning and experimentation on day 12, the device unfortunately became unusable. Sensitivity could not be confirmed. The insertion loss rose above the experimental threshold of 35 dB, resulting in extremely high noise and making the device unusable. The device was taken out of the flow cell and observed under a microscope. This drastic increase in loss was due to the accumulation of pinholes in the coating on the surface of the device. The pinholes in the coating extended to the surface of the device allowing water to come in contact with the IDTs and the sensing area of the device. This caused extreme attenuation of the SH-SAW and increased the loss drastically.

4.3.3   Third blend (24.4% DINCH-PS)

The plasticizer percentage was decreased to 24.4% to maintain an increased sensitivity over the 20.9% DINCH-PS coating and increase the stability over the 26.2% DINCH-PS coating. The coating thickness was increased to 1.3µm to maintain high sensitivity. The initial insertion loss was 28.4 dB. This high insertion is due to the thickness of the coating and also suggests the coating is rubbery. This indicates that there should be significant sensitivity to benzene. The frequency response to benzene is shown in Figure 12. The sensor was stable for around 20 days. On day 26, the noise level was extremely high. This is due to the insertion loss reaching the threshold level of 35 dB. The noise level was too high to continue past day 26; it was observed that the sensor response on day 26 does not match up with previous data. When the sensor loss reaches this threshold empirically determined, not only is the noise high, but the sensor response becomes unreliable.

Figure 12: Overlaid frequency responses of a 1.3µm-thick 24.4% DINCH-PS coated SH-SAW sensor normalized to 1 ppm benzene with a 30% weighted fit to smooth noise [Note that data taken after day 20 was not included because the measured device loss at the operating frequency was above the 35 dB threshold].

4.3.3.1 Sensitivity

The frequency responses were extracted and plotted as a function of benzene

concentration. A linear fit was performed to extract the sensitivity of the sensor coating

to benzene.

Figure 13: Measured frequency shifts as a function of benzene concentrations with a linear fit to extract sensitivity for a 1.3µm-thick 24.4% DINCH-PS coated SH-SAW sensor.

The sensitivity of benzene was determined to be 0.539 Hz/ppb from Figure 13.

The sensitivity of the 1.3µm-thick 24.4% DINCH-PS sensor to benzene was significantly

higher than that of the 0.8µm-thick 20.9% DINCH-PS sensor. The high initial insertion

loss of the 1.3µm-thick 24.4% DINCH-PS sensor gives rise to a higher level of noise (16.7

Hz) over the 0.8μm-thick 20.9% DINCH-PS sensor (3.6 Hz). Considering noise, the limit of detection of the 1.3μm-thick 24.4% DINCH-PS coated sensor for benzene was determined to be 95 ppb.

The goal was to find a coating with a detection limit lower than 100 ppb, which the 24.4% DINCH-PS sensor coating satisfies. Though the 24.4% DINCH-PS sensor coating satisfies the condition of low detection limit, the large increase in sensitivity from the 20.9% DINCH-PS sensor coating would suggest a large improvement in the limit of detection for benzene. It shows that even though sensitivity was greatly increased (8.5 times greater), the increase in noise (4.6 times greater) plays a large role in the ability to detect low concentrations (detection limit only reduced by 44%).

4.3.3.2 Stability

The coated device insertion loss at the operation point was tracked and plotted in Figure 14. The initial insertion loss was high and the rate of loss increase allowed for sensing for three weeks. The sensor response had a fairly large spread. As the loss increased over time, the sensor noise also increased. The noise on day 26 was extremely high. On day 26, the insertion loss was 35.6 dB which is above the threshold for experimentation. Data taken above the threshold is unreliable and is subjected to a very high level of noise that affects the limit of detection of a sensor. The ideal sensor coating needs to be sensitive with a low noise level to be able to detect concentrations of benzene under 100 ppb while maintaining long-term stability. Due to the short span of sensor stability, further adjustment of the plasticizer percentage was investigated.

Figure 14: Device insertion loss at the operating frequency for the 1.3µm-thick 24.4% DINCH-PS SH-SAW sensor coating tracked over a period of 20 days.

4.3.4 Fourth blend (23.0% DINCH-PS)

The plasticizer percentage was lowered to 23.0% DINCH to increase the stability

of the sensor. The resulting coating thickness was measured to be 1.0µm. This

plasticizer-polymer ratio was found to be the best from this work. It combined high

sensitivity with good stability. The normalized frequency responses of the sensor to

benzene are shown in Figure 15.

Figure 15: Overlaid measured frequency responses of the 1.0µm-thick 23.0% DINCH-PS coated SH-SAW sensor normalized to 1 ppm benzene with a 30% weighted fit to smooth noise [Note: data shows repeatability of sensor frequency response]

4.3.4.1 Sensitivity

The frequency shift was extracted from the raw data and was plotted as a function of the benzene concentration. The slope of this calibration curve was used to determine the sensitivity of the coating to benzene.

Figure 16: Measured frequency shifts as a function of benzene concentrations with a linear fit to extract sensitivity for a 1.0μm-thick 23.0% DINCH-PS coated SH-SAW sensor.

The sensitivity to benzene was found to be 0.304 Hz/ppb from Figure 16. After extracting the noise levels from the baseline (8.85 Hz), the limit of detection was determined to be 85 ppb. The observed sensitivity is lower than that of the 1.3μm-thick

24.4% DINCH-PS coated sensor, but due to the lower noise level, a lower detection limit is obtained. The detection limit for the 1.0μm thick 23.0% DINCH-PS coated sensor is within the goal for this project.

4.3.4.2 Stability

To determine the stability of the device, the loss at the operating frequency was tracked and the repeatability of the sensor response was investigated. The initial insertion loss was 21.9 dB. The loss was tr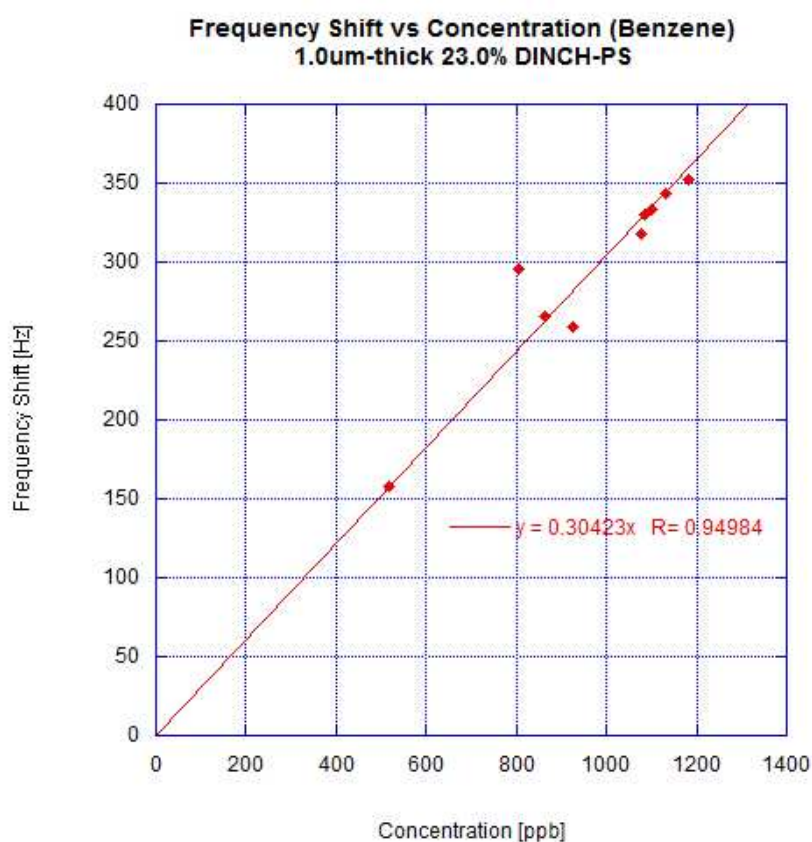acked at the operating frequency at the beginning of each experiment for 57 days. After day 57, measurements were halted due to perturbation from construction work within the building. The sensor response was affected by the construction perturbations and any data taken after the construction process began was not used. As seen in Figure 17, the loss tracking shows stability for nearly two months and when extrapolated, suggests stability for over 100 days before the loss reaches the threshold for experimentation (35 dB). The sensor response over the two months was repeatable and the spread in sensor responses was small.

Figure 17: Device insertion loss at the operating frequency for the 1.0μm-thick 23.0% DINCH-PS SH-SAW sensor coating tracked over a period of two months.

4.3.4.3 Reproducibility and repeatability

The 1.0μm-thick 23.0% DINCH-PS coated sensor showed stability and good

sensitivity. The sensor was replicated to confirm sensor reproducibility. The results of

the second 23.0% DINCH-PS coated sensor are shown in Figure 18, 19 and 20. The

frequency data between day 5 and day 80 was excluded because of issues with the flow

cell. There was debris in the inlet and outlet line of the flow cell chamber. This caused

air bubbles to get stuck in the inlet line causing back pressure. This back pressure due to

various bubble sizes on various experimental days affected the sensor response causing a large spread of frequency response data. When the cause of the problem was found, the flow cell was taken apart, the tubes were replaced and the inlet and outlet lines were cleaned of debris.

The sensor was put back into the cell. Since the sensor coating was not damaged beyond use (loss was still under 35 dB), the device was used to continue tracking loss data and measuring frequency response. Though frequency data between day 5 and 80 was not used, the unaffected data between days 81 and 116 showed stability and reproducibility that matched, within error, the original 23.0% DINCH-PS coated sensor data. As the device aged, it was observed that the sensitivity changed. The data on day 166 and 173 showed about a 50% decrease in sensitivity, indicating degradation of the sensor coating.

Figure 18: Overlaid frequency responses of the reproduced 1.0μm-thick 23.0% DINCH-PS coated SH-SAW sensor normalized to 1 ppm benzene with a 30% weighted fit to smooth noise [Data taken after day 116 were not included due degradation of the sensor response]

The frequency shift was extracted from the raw data and plotted as a function of the benzene concentration. The slope of this calibration curve was used to determine the sensitivity. The sensitivity of the reproduced device was determined to be 0.237 Hz/ppb from the average of data up to day 116 shown in Figure 19.

Figure 19: Measured frequency shift as a function of benzene concentration with a linear fit to extract sensitivity for the reproduced 1.0μm-thick 23.0% DINCH-PS coated SH-SAW sensor.

The first 23.0% DINCH-PS device was operating in the loss range of 22 to 28 dB and the reproduced device was in the range of 25 to 33 dB. This higher loss range for

the reproduced device can affect the sensor's noise level. As the device aged, the

insertion loss also increased. Loss tracking for the reproduced device is shown in Figure

20. This decreases the limit of detection. Based on the noise measurement on day 5 of

the reproduced 1.0µm-thick 23.0% DINCH-PS sensor (6.4 Hz), the detection limit was 82

ppb. The loss on day 5 was in the range of the first device and the detection limit

matches that of the first device and supports, along with the similar sensitivity to

benzene, that the coated sensor device can be reproduced within the error expected
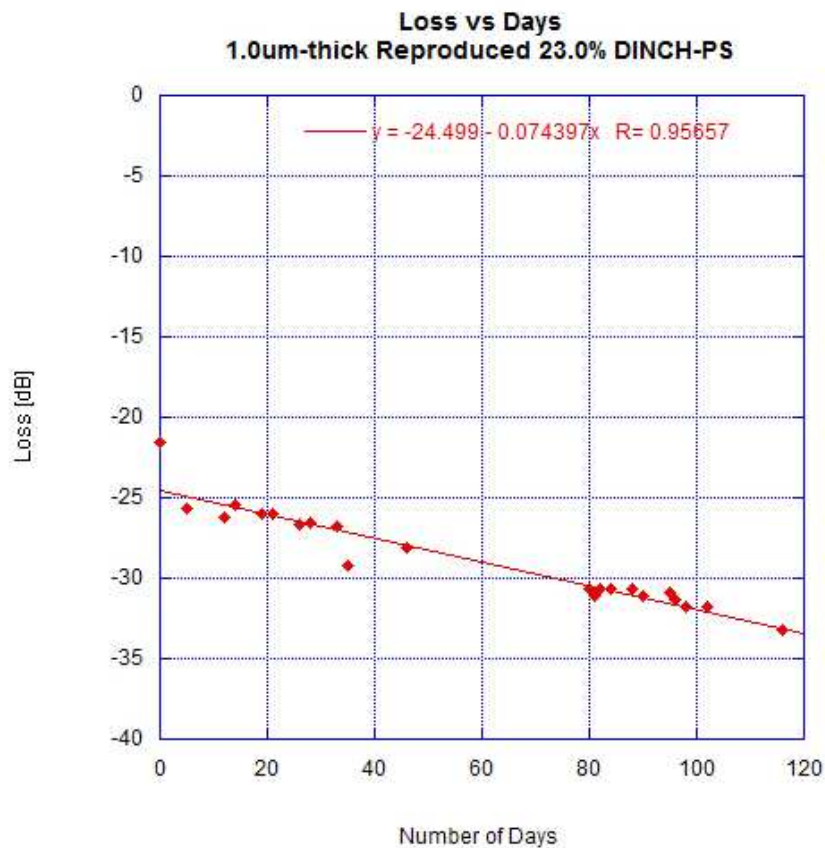
due to the manual fabrication of the coating.

Figure 20: Device insertion loss at the operating frequency for the reproduced 1.0µm-thick 23.0% DINCH-PS SH-SAW sensor coating tracked for a period of 116 days.

4.3.4.4   Effect of thickness variation

The insertion loss in the lower 20 dB range for the 1.0μm thick 23.0% DINCH-PS coating suggests that the thickness could be increased slightly. This may allow for an increased sensitivity while still maintaining high long-term stability. The thickness of the 23% DINCH-PS coating was increased to 1.2 and 1.3μm. The plasticizer percentages were 23 %. Clearly, increasing thickness results in larger sensitivities compared to the 1.0μm- thick coating, but both devices were not stable. The 1.2μm-thick device lasted less than two weeks and both of the 1.3μm-thick devices lasted one day. The devices were observed under the microscope and pinholes in the coating were discovered after instability was determined.

4.4   Pinhole formation

Most sensor devices showed formation of pinholes over the course of their use. The rate of formation and detrimental effects varied between sensor coatings. Pinholes are typically formed due to contamination of organic material on the surface of the device before coating. This contamination affects the adhesion of the polymer coating to the surface of the device. The points of contamination do not allow for the polymer to adhere to the surface and over time, the polymer will retract from the contamination, leaving a pinhole. Additional cleaning steps were added to the device preparation to try and eliminate this problem after pinhole formation was noticed. Though additional cleaning steps were added, pinholes were still forming. This could still be partially due to

contamination since devices are not prepared in a clean room environment. Another possible explanation for the pinhole formation is the concentration of plasticizer.

As the plasticizer percentage was increased, so did the rate of formation of pinholes. The 26.2% DINCH-PS sensor coating degraded within two experimentation days over two weeks' time. Higher plasticizer percentage increases the free volume allowing for higher sensitivity, but also increases the mobility of the polymer molecules. This higher mobility may contribute to the faster formation of pinholes. With polymer molecules moving more easily, inhomogeneities start to occur, and over time, holes are formed. Coatings with higher plasticizer percentages degraded faster than those with lower concentrations. The 24.4% DINCH-PS sensor coating lasted around one month before the coating degraded. The 20.9% DINCH-PS sensor coating never degraded to the point of sensor failure, but after two months, some degradation was visible. No pinholes were observed, but there was some surface stress from swelling and drying as well as some debris deposits visible under the microscope. The lack of pinhole formation supports the conclusion that the 20.9% DINCH-PS sensor coating was glassier. A glassy coating is more rigid and would be more resistant to the formation of pinholes.

The best plasticizer percentage found in this work (around 23% DINCH) showed the formation of pinholes when viewed under the microscope, but never developed fully enough to cause high increases in loss. It appeared that the pinholes did not go deep enough into the coating to reach the surface of the device. With no water contact to the substrate surface, the SH-SAW was not highly attenuated.

4.5   Selectivity

Once the ideal DINCH-PS coating was determined for the detection of benzene (as the 1.0µm thick 23.0% DINCH-PS coating), the other BTEX compounds were investigated. Normalized frequency responses to toluene, ethylbenzene and xylene are shown in Figure 21, 22 and 23, respectively. A baseline correction for drift was made in plotting the data.

Figure 21: Overlaid frequency responses of the reproduced 1.0µm-thick 23.0% DINCH-PS coated SH-SAW sensor normalized to 1 ppm toluene [Note: data shows repeatability of sensor frequency response]

Figure 22: Overlaid frequency responses of the reproduced 1.0μm-thick 23.0% DINCH-PS coated SH-SAW sensor normalized to 1 ppm ethylbenzene [Note: data shows repeatability of sensor frequency response - Day 96 is an outlier from preconditioning of the coating to ethylbenzene]

Figure 23: Overlaid frequency responses of the reproduced 1.0µm-thick 23.0% DINCH-PS coated SH-SAW sensor normalized to 1 ppm xylene [Note: data shows repeatability of sensor frequency response]

The frequency shift was extracted from the raw data and plotted as a function of the analyte concentration. The slope of this calibration curve was used to determine the sensitivity of the sensor to each analyte. The curves for toluene, ethylbenzene and xylenes are respectively shown in Figured 24, 25, and 26.

Figure 24: Measured frequency shifts as a function of toluene concentrations with a linear fit to extract sensitivity for the reproduced 1.0µm-thick 23.0% DINCH-PS coated SH-SAW sensor.

Figure 25: Measured frequency shifts as a function of ethylbenzene concentrations with a linear fit to extract sensitivity for the reproduced 1.0μm-thick 23.0% DINCH-PS coated SH-SAW sensor.

Figure 26: Measured frequency shifts as a function of xylene concentrations with a linear fit to extract sensitivity for the reproduced 1.0µm-thick 23.0% DINCH-PS coated SH-SAW sensor.

The sensitivities of toluene, ethylbenzene and xylene were 0.810 Hz/ppb, 2.009

Hz/ppb and 2.521 Hz/ppb, respectively. Considering the measured noise (toluene: 14.6

Hz, ethylbenzene: 17.2 Hz, and xylenes: 16.1 Hz), the limit of detection was determined

to be 55 ppb, 25 ppb and 20 ppb for toluene, ethylbenzene and xylenes, respectively.

Data on partial selectivity of the 23.0% DINCH-PS reproduced sensor coating is shown in

Figure 27 compared to commercially available polymers that have been investigated as

chemically sensitive sensor coatings for BTEX compounds. Sensitivities are normalized

with respect to the benzene sensitivity, analyte molecular weight and analyte solubility

in water. The difference in selectivity of each sensor coating would allow for a sensor

array to be implemented to identify and quantify BTEX compounds in a sample.

Figure 27: Partial selectivity comparison between sensor coatings normalized with respect to benzene concentration, analyte molecular weight and analyte solubility in water

4.6 Sensitivity Comparison

One of the goals of this work was to determine a suitable plasticizer-polymer

blend to be used as a sensor coating with high sensitivity. A comparison of the

investigated DINCH-PS blend sensitivities and the detection limits to benzene are shown

in Table 3.

DINCH-PS Coating (Plasticizer %)	Thickness (µm)	Sensitivity (Hz/ppb)				Benzene Detection Limit (ppb)
		Benzene	Toluene	Ethylbenzene	Xylenes	
20.9%	0.8	0.0632	NA	NA	NA	170
23.0%	1.0	0.304	NA	NA	NA	85
23.0% (Reproduced)	1.0	0.237	0.810	2.009	2.521	82*
24.4%	1.3	0.539	NA	NA	NA	95

Table 3: Summary of DINCH-PS SH-SAW sensor coatings showing sensitivity to BTEX and the detection limit for benzene

Figure 28 shows a comparison of the measured frequency shifts as a function of

benzene concentrations for the 20.9% DINCH-PS, 23.0% DINCH-PS and the 24.4%

DINCH-PS sensor coatings compared to previously studied plasticizer-polymer blend

coatings and polymer coatings on a SH-SAW sensor [23]. A linear fit was added to each

set of data to show sensitivity. Steeper slope represents a larger sensitivity of the

coating to benzene. From Figure 28, the coating with highest reported sensitivity to

benzene was the 23% DOP-PS (1.12μm) coating [36] followed by the 24.4% DINCH-PS

coating studied in this work.

Figure 28: Comparison of frequency shift as a function of benzene concentration between investigated DINCH-PS sensor coatings and previously studied SH-SAW sensor coatings

The stability of DOP-PS blends was not investigated in great depth, but initial stability testing of the 23.4% DOP-PS coating suggests DOP-PS is not suitable for long term measurements due to an increased loss over the threshold of 35 dB after 10 days. Previous investigation of PECH coatings has determined the polymer to be a suitable sensor coating with sufficient stability [24]. PEA was determined to be a sensitive sensor coating to benzene [23], but was found to be unstable over time when in the presence of water. Figure 28 shows that the investigated DINCH-PS sensor coating in this work (23.0% DINCH-PS at 1.0µm) has a relatively high sensitivity compared to the commercially available polymers used as stable coatings for detection of BTEX compounds. Out of the stable sensor coatings, the 23.0% DINCH-PS sensor coating has the largest sensitivity.

4.7   Time Constant

When the frequency response curve was fitted, the frequency shift and time constant were extracted. It should be noted that the time to reach steady state (time response) and time constant are two different parameters as described in chapter 1. Though the focus of this work was on sensitivity and stability, time responses were extracted for all DINCH-PS blend sensor coatings. A summary of Time constants are shown in Table 4.

DINCH-PS Coating (Plasticizer %)	Thickness (µm)	Time Constant τ (seconds)			
		Benzene	Toluene	Ethylbenzene	Xylenes
20.9%	0.8	66.8	NA	NA	NA
23.0%	1.0	71.4	NA	NA	NA
23.0% (Reproduced)	1.0	69.6	140.4	363.9	358.1
24.4%	1.3	73.6	NA	NA	NA

Table 4: Summary of DINCH-PS SH-SAW sensor coatings showing time constants for the absorption of BTEX.

Time constants for the benzene are comparable between sensor coatings. There will be slight variation due to the difference in plasticizer percentage and coating thickness. The time constant for benzene was averaged for the two 23.0% DINCH-PS coatings and was determined to be 70.5 seconds. The results in Table 4 show a distinct time constant for benzene, toluene and ethylbenzene/xylene. Ethylbenzene and xylene have very similar time constants and are typically grouped together in multiple analyte mixture analysis. The distinction between the analyte time constants and sensitivities allows for the identification and quantification of BTEX in a sample.

5   Summary, Conclusions and Future Work

5.1   Summary

The goal of this work was to develop a suitable plasticizer-polymer sensor coating for in-situ, long term monitoring of water for BTEX compounds. The sensor device used a three-layer geometry on a shear horizontal surface acoustic wave sensor platform. The plasticizer-polymer coating investigated was a DINCH-PS blend. Various plasticizer concentrations (measured as a weight/weight percentage) and coating thicknesses were studied to characterize sensitivity, repeatability, long-term stability and reproducibility. Plasticizer concentration affects the glass transition temperature of the polymer which defines the state of the polymer during the experiments. Higher plasticizer concentrations produce lower glass transition temperatures creating a more rubbery coating. A rubbery coating has higher sensitivity, but decreased long term stability. In the present work, a suitable plasticizer-polymer coating was determined to be a 1.0μm-thick 23.0% DINCH-PS sensor coating. The 23.0% DINCH-PS sensor coating had high sensitivity to benzene (averaged at 270 Hz/ppm) with repeatability over a period of three months. Sensitivities to toluene, ethylbenzene and xylene were 810 Hz/ppm, 2.0 kHz/ppm and 2.5 kHz/ppm, respectively.

The background of the problem was initially introduced to emphasize the need for an in-situ sensor to improve the current method of analysis. An overview of chemical sensors was discussed with focus on acoustic wave sensors. Characteristics of various acoustic wave sensors were compared to explain the choice of a shear horizontal surface acoustic wave (SH-SAW) device as the sensor platform used in this project. The

SH-SAW device was chosen due to the high sensitivity to surface perturbations, the ability to be used in an aqueous environment and the physical robust nature of the device design. Theory of the SH-SAW was reviewed and discussed in great detail to explain how the device responds to the measurand. Polymer properties and solubility were defined and multiple theories on plasticization were introduced (lubricity theory, gel theory, and free volume theory). The plasticization process and the effects on glass transition temperature are necessary components in determining proper plasticizer concentration for sensor coatings.

Various concentrations of DINCH were investigated (20.9%, 23.0%, 24.4%, and 26.2%) to determine the appropriate concentration and the effects on long term stability. Device preparation, coating preparation, coating deposition and experimental methods were provided and precisely followed. Experiments were performed to determine the sensitivity, repeatability and stability of the DINCH-PS blends as sensor coatings. The device insertion loss was tracked at the experimental operating frequency to track any degradation of the coating that affects the signal noise or frequency response. Measured frequency responses from different time (i.e. days) were normalized to the corresponding analyte concentration measured by the GC-PID to determine repeatability of the sensor response over a period of experimental days. Sensitivity to benzene and the benzene detection limit for each DINCH-PS blend sensor coating was calculated using the measured noise.

Once a sensitive, stable coating was determined, frequency responses to the other BTEX compounds were measured. Sensitivity and detection limit for the other

compounds (TEX) were also calculated using the appropriate measured noise. An identical coating was reproduced and repeated experiments were conducted to confirm findings and show reproducibility between the two 23.0% DINCH-PS sensor coatings.

Data processing and analysis was conducted in the same manner for all sensor coatings. Sensor frequency responses were corrected for baseline drift, measured frequency response was normalized to the concentration of analyte determined by the GC-PID, and frequency shifts and response times were extracted using the same fitting program in Matlab. Sensitivity and detection limit of benzene for each DINCH-PS blend sensor coating and sensitivity to toluene, ethylbenzene and xylene for the 23.0% DINCH-PS reproduced sensor coating were summarized in Table 3.

5.2 Conclusions

The low plasticizer percentage of 20.9% DINCH gave a very stable coating that was, however, determined to be too glassy. The sensitivity to benzene was very low (60 Hz/ppm) and a low sensor noise gave a detection limit of benzene as 170 ppb. An increase of the thickness while maintaining the same plasticizer concentration should increase the sensitivity, but the results and measured insertion loss of 19.8dB suggest that the coating is still relatively glassy.

When the plasticizer concentration was increased to 26.2% DINCH with a thickness of 1.0µm, the coating was determined to be unstable. The initial insertion loss was 23.4dB which gives over 10dB of loss before the sensor reaches the experimental insertion loss threshold for high noise (35dB). Initial experimentation showed high

sensitivity, but after a short period of time (two experimental days), the coating was covered in pinholes that scattered the acoustic wave and allowed for water to interact with the surface of the SH-SAW device. This attenuated the SH-SAW, increased the insertion loss above operating levels (35 dB), and hence making the sensor no longer usable.

Decreasing the plasticizer concentration to 24.4% DINCH and increasing the thickness to 1.3µm allowed for a sensitivity to benzene of 400Hz/ppb. The initial insertion loss for the 24.4% DINCH-PS sensor coating was on the high side (28.4 dB), though still within operating range. Decreasing the thickness while maintaining the same concentration would lower the initial insertion loss, allowing for longer use, but would come at a cost of decreasing the sensitivity. The coating was stable for around three weeks before the insertion loss became too high (>35dB) for experimentation. Frequency response data taken after this point had very high noise and were unreliable.

Decreasing the plasticizer concentration showed a trend towards stability. As a result, a percentage between 20.9% DINCH and 24.4% DINCH was chosen. The next coating investigated was a 1.0µm-thick 23.0% DINCH-PS sensor coating. This blend was determined to be the best concentration of DINCH for a sensor coating using polystyrene found in this work. The device was stable for around three months yielding repeatable frequency response. The sensor coating was reproduced and was determined to be repeatable within error of the plasticizer concentration and coating thickness. Frequency response to all BTEX compounds was characterized with respect to the sensitivity to each individual analyte, and the respective detection limit. Sensitivity

to each BTEX analyte was determined to be 270 Hz/ppm, 810 Hz/ppm, 2.0 kHz/ppm and

2.5 kHz/ppm, respectively. With noise considerations, the detection limits of each BTEX

analyte was determined to be 85 ppb, 55 ppb, 25 ppb, and 20 ppb, respectively.

The results demonstrate that it is possible to make a glassy polymer, such as

polystyrene, a suitable sensor coating for BTEX detection in an aqueous environment

with enhanced long-term stability by the addition of a plasticizer. By careful choice of a

plasticizer with low leaching rate in water, appropriate plasticizer concentration and

coating thickness, a sensor coating with the desired characteristics was obtained.

DINCH-PS blend sensor coatings will be a valuable contribution to a sensor array for

detection of low concentrations of benzene in long-term groundwater monitoring

measurements.

5.3   Future work

The research conducted in this work has shown the validity of a stable DINCH

plasticized polystyrene SH-SAW coating for the detection of BTEX compounds in an

aqueous environment. Though the plasticizer percentage was optimized, further

refinement of the plasticizer percentage and coating thickness is needed to be able to

adjust the sensitivity and stability for specific applications. For example, some

applications may require a very high sensitivity and may not require months of stability,

while other applications may require to sacrifice sensitivity for a sensor that is stable for

extremely long periods of time. A more refined tuning of the plasticizer percentage and

coating thickness could allow the user to adjust the ideal coating for their specific

sensing application.

The goal of the overall project is to create a sensor array to identify and quantify the presence of BTEX in groundwater. This requires multiple coatings that uniquely respond to these compounds. Investigation of other possible sensor coatings is of interest to the entire project. The addition of a plasticizer has been previously shown to increase the sensitivity of a polymer as a chemical sensor coating. In previous work, the various plasticizer-polymer combinations were not studied for long term use. Some combinations of plasticizer-polymers show more promise than others, and their long term stability and reproducibility could be investigated as an extension of this work to determine other ideal sensor coatings. The ability to tune the plasticizer concentration for the specific application makes for a more versatile sensor array.

Over the course of this work, a major problem was found to occur for all coating mixtures. There was an adhesion problem that was resulting in the degradation of the sensor coating in the form of pinholes. Plasticizer concentration and coating thickness appeared to have an effect on the rate and degree of coating degradation. Investigation of this correlation could be examined further to try and reduce/eliminate the problem. Other means to improve adhesion may be investigated, such as the use of a polystyrene sample with higher molecular weight or the addition of an adhesion promoter, to help improve the stability of the sensor coatings. Reduced polymer creep or improved adhesion may result in longer stability of each coating, allowing for a higher plasticizer percentage or larger thickness to be used, which can greatly improve the sensitivity to BTEX even further.

REFERENCES

[1] U.S. Geological Survey, "Environmental Health - Toxic Substances: BTEX," U.S. Department of the Interior, 04 August 2015. [Online]. Available: http://toxics.usgs.gov/definitions/btex.html.

[2] United States Environmental Protection Agency, "Ground-Water Monitoring Technical Enforcement Guidance Document," 20 February 2015. [Online]. Available: http://www.epa.gov/enforcement/rcra-ground-water-monitoring-technical-enforcement-guidance-document-tegd. [Accessed 11 January 2016].

[3] D. Pope, S. Acree, H. Levine, S. Mangion, J. Van Ee, K. Hurt and B. Wilson, "Performance Monitoring of MNA Remedies for VOCs in Ground Water," Agency, United States Environmental Protection, Cincinnati, OH, 2004.

[4] EPA, "Background on Drinking Water Standards in the Safe Drinking Water Act (SDWA)," Environmental Protection Agency, 7 December 2015. [Online]. Available: www.epa.gov/dwstandardsregulations/background-drinking-water-standards-safe-drinking-water-act-sdwa. [Accessed 7 December 2015].

[5] EPA, "National Primary Drinking Water Regulations," United States Environmental Protection Agency, May 2009.

[6] EPA, "Semiannual Report of UST Performance Measures End of Fiscal Year 2014," Office of Underground Storage Tanks, Washington, D. C., 2014.

[7] J. S. Wilson, Ed., Sensor Technology Handbook, Burlington, MA: Elsevier Inc., 2005.

[8] J. Stetter, W. Penrose and S. Yao, "Sensors, Chemical Sensors, Electrochemical Sensors, and ECS," *Journal of the Electrochemical Society,* vol. 150, pp. S11-S16, 2003.

[9] A. K. Mensah-Brown, *Detection of organophosphates in the liquid-phase using guided SH-SAW sensors, MS Thesis,* Milwaukee: Marquette, 2007.

[10] F. Bender, F. Josse and A. Ricco, "Influence of Ambient Parameters on the Response of Polymer-Coated SH-Surface Acoustic Wave Sensors to Aromatic Analytes in Liquid-Phase Detection," in *Joint Conference of the IEEE International Frequency Control Symposium & European Frequency and Time Forum Proceedings*, San Francisco, CA, 2011.

[11] Wikipedia, "Time Constant," 8 April 2016. [Online]. Available: https://en.wikipedia.org/wiki/Time_constant. [Accessed April 2016].

[12] H. Campanella, Acoustic Wave and Electromechanical Resonators: Concept to Key Applications, Boston: Artech House, 2010.

[13] B. Drafts, "Acoustic Wave Technology Sensors," *IEEE Transactions on Microwave Theory and Techniques,* vol. 49, pp. 795-802, 2001.

[14] D. Ballantine and et al, Acoustic Wave Sensors - Design, Theory and Physico-Chemical Applications, Elsevier, 1997.

[15] "The Piezoelectric Effect," Nanomotion Johnson Electric, 2008-2015. [Online]. Available: http://www.nanomotion.com/piezo-ceramic-motor-technology/piezoelectric-effect/. [Accessed October 2015].

[16] J. Hossenlopp, *Applications of Acoustic Wave Devices for Sensing in Liquid Environments,* Milwaukee: Marquette University, 2006.

[17] C. White, B. Pejcic, M. Meyers and X. Qi, "Development of a plasticizer-poly(methyl methacrylate)membrane for sensing petroleum hydrocarbons in water," *Sensors and Actuators B,* no. 193, pp. 70-77, 2014.

[18] B. Pejcic, E. Crooke, L. Boyd, C. Doherty, A. Hill and M. Myers, "Using Plasticizers to Control the Hydrocarbon Selectivity of a Poly(Methyl Methacrylate)-Coated Quartz Crystal Microbalance Sensor," *Analytical Chemistry,* vol. 84, p. 8564–8570, 2012.

[19] L. Rayleigh, "On Waves Propagated along the Plane Surface of an Elastic Solid," *Proceedings of the London Mathematical Society,* pp. 4-11, 1885.

[20] T. Newman, *Analysis of the detection of organophosphate pesticides in aqueous soulstions using polymer-coated SH-SAW sensor arrays, MS Thesis,* Milwaukee, WI: Marquette University, 2012.

[21] T. Newman, F. Josse, A. Mensah-Brown and F. Bender, "Analysis of the Detection of Organophosphate Pesticides in Aqueous Solutions Using Polymer-Coated SH-SAW Sensor Arrays," in *European Frequency and Time Forum & International Frequency Control Symposium (EFTF/IFC)*, Prague, 2013.

[22] R. Lenisa, *Chemically senistive polymer coatings for SH-surface acoustic wave sensors for the detection of benzene in water, MS Thesis,* Milwaukee, WI: Marquette University, 2013.

[23] F. Bender, R. Mohler, A. J. Ricco and F. Josse, "Quantification of Benzene in GroundwaterUsing SH-Surface Acoustic Wave Sensors," pp. 473-476, 2012.

[24] F. Bender, F. Josse, R. Mohler and A. Ricco, "Design of SH-Surface Acoustic Wave Sensors for Detection of ppb Concentrations of BTEX in Water," *IEEE IFCS,* pp. 628-631, 2013.

[25] G. Kovacs and et. al., "Improved Material Constants for LiNb03 and LiTaO3," *Ultrasonics Symposium,* pp. 435-438, 1990.

[26] *F. Josse at Marquette University and R. Cernosek at Sandia National Laboratories.*

[27] Z. Li, *Guided Shear-Horizontal Surface Acoustic Wave (SH-SAW) Chemical Sensors for Detection of Orgaic Contaminants in Aqueous Environments, Dissertation,* Milwaukee, WI: Marquette University, 2005.

[28] K. Hashimoto, Surface Acoustic Wave Devices in Telecommunications, Berlin: Springer, 2000, p. 48.

[29] N. Naumenko, "Multilayered Structure as a Novel Material for Surface Acoustic Wave Devices: Physical Insight," in *Acoustic Waves – From Microdevices to Helioseismology*, Shanghai, Intech, 2011, p. 422.

[30] D. Hollar Jr., Salem Press Encyclopedia of Science, Salem, 2011.

[31] J. Burke, "Solubility Parameters: Theory and Application," 3 August 2011. [Online]. Available: http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html. [Accessed 16 November 2015].

[32] C. M. Hansen, "Solubility Parameters — An Introduction," in *Hansen Solubility Parameters: A User's Handbook*, CRC Press LLC, 2000 .

[33] D. Icoz, Understanding Molecular and Thermodynamic Miscibility of Carbohydrate Biopolymers, Ann Arbor, MI: ProQuest LLC, 2008.

[34] T. Crompton, United Kingdom: Rapra Technology Limited, 2006.

[35] M. Aklonis, Introduction to Polymer Viscoelasticity, John Wiley and Sons, 1983.

[36] J. Coompson, *Characterization of plasticizer-polymer coatings, Thesis,* Milwaukee, WI: Marquette University, 2015.

[37] e. George Wypych, Handbook of Plasticizers 2nd Edition, Toronto: ChemTech Publishing, 2012.

[38] J. Kastner, D. Cooper, M. Maric, P. Dodd and V. Yargeau, "Aqueous leaching of di-2-ethylhexyl phthalate and "green" plasticizers," *Science of the Total Environment,* no. 432, pp. 357-364, 2012.

[39] C. White, B. Pejcic, M. Meyers and X. Qi, "Development of a plasticizer-poly(methyl methacrylate)membrane for sensing petroleum hydrocarbons in water," *Sensors and Actuators B,* no. 193, pp. 70-77, 2014.

[40] G. Wypych, Handbook of polymers, ChemTec Pub., 2012.

[41] BASF, *Corresponding email on DINCH solubility parameters,* 2015.

[42] "Solvent Blends," 2015. [Online]. Available: www.Hansen-Solubility.com/SolventBlends.html. [Accessed 30 November 2015].

[43] F. Josse, F. Bender and R. Cernosek, "Guided shear horizontal surface acoustic wave sensors for chemical and biochemical detection in liquids," *Analyitical Chemistry,* vol. 73, pp. 5937-5944, 2001.

[44] Z. Li, Y. Jones, J. Hossenlopp, R. Cernosek and F. Josse, "Analysis of liquid-phase chemical detection using guided shear horizontal-surface acoustic wave sensors," *Analytical Chemistry,* vol. 77, pp. 4595-4603, 2005.

[45] Sigma-Aldrich, "Dioctyl phthalate - Specification Sheet," [Online]. Available: http://www.sigmaaldrich.com/Graphics/COfAInfo/SigmaSAPQM/SPEC/D2/D201154/D201154-BULK_____ALDRICH__.pdf.

[46] BASF, "Hexamoll DINCH - Technical Information," February 2015. [Online]. Available: http://www.plasticizers.basf.com/portal/load/fid247503/Hex_DINCH_e_11_14.pdf.

[47] D. Technologies, "Hand-Held Gas Chromatography," Defiant Technologies, 2015. [Online]. Available: www.defiant-tech.com/frog-4000.php. [Accessed 17 November 2015].