RFID Tags / Planar Inductors as Chemical Sensor Platforms in Liquid Sensing Applications

Gregory Donald Schumacher-Novak
Marquette University

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RFID Tags / Planar Inductors as Chemical Sensor Platforms in Liquid Sensing Applications

By

GREGORY D. NOVAK

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ABSTRACT
RFID TAGS / PLANAR INDUCTORS AS CHEMICAL SENSOR PLATFORMS IN LIQUID SENSING APPLICATIONS

Gregory D. Novak

Marquette University, 2009

In this work, RFID tags are investigated as a liquid-phase chemical sensing platform. A dual-layer of selective coating film with polyaniline (PANi) on top of poly(epichlorohydrin) (PECH) is used for the detection of trace amounts of organic compounds (toluene and ethylbenzene) in aqueous solutions. Various experiments were performed to evaluate the coated RFID tag sensors. Shifts in the impedance and resonant frequency due to analyte sorption are measured. Details of the responses of the dual-layer film to different pH baseline solutions are shown. The results show that this dual-layer film can be used to detect toluene and ethylbenzene with high sensitivity. The conductive nature of PANi when protonated with an acidic solution allowed for increased sensitivity.

To describe the observed changes that occur during detection, an equivalent circuit model of the RFID tag chemical sensor was developed. The derived equations could be used to describe the observed response due to chemical sorption. The addition of PANi provided added sensitivity as the traces of the planar inductor began to effectively short out with increasing conductivity of the polymer. This is due to the different level of protonation of PANi that occurs. Lower pH solutions result in an increase in the conductivity of PANi to a level that drastically changes the characteristics of the coil (number of turns and width of the traces), thus shifting the operating resonant frequency. The large shift in frequency is related to a decrease in both the inductance and the capacitance of the coil. However, this shift would cause the tag to no longer operate with the reader. The results with the aqueous baseline solution of pH = 1 provides the largest sensitivity; however, the results with the aqueous baseline solution of pH = 3.5 also provides highly sensitive responses. Partial selectivity of the coated sensor was also found to be a function of the solution pH, thus the protonation of the PANi. For the present study, a limit of detection with a baseline solution of pH = 3.5 was found to be 6.24 ppb and 8.3 ppb for toluene and ethylbenzene, respectively.

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“Nearly every man who develops an idea works it up to the point where it looks impossible, and then he gets discouraged. That's not the place to become discouraged.”

Thomas Edison

There have been various points where this work has seemed impossible, but there have been plenty of people who have been there encourage me to get past that point. This work is dedicated to all those that have supported me through the ups and down that have come throughout this entire process. Thank you for all that you have given me, including all of the great pieces of advice and tremendous support!

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1 INTRODUCTION

1.1 Background

Chemicals have useful applications, but can be harmful depending on both the type and the concentration. For example, chemical contamination of ground and waste water can result in hazardous water that can affect many components of human life. To ensure the health of the general public concerning the presence of these chemicals in various solutions, it is necessary to test or monitor the environment for the concentration and types of any harmful substances.

Traditional analytical methods for gas and liquid phase chemical detection are slow and inefficient. This leads to the need for improving the detection process of these chemicals to ensure the safety of the general public. There are currently different sensing platforms available for chemical sensing in liquid environments. However, they result in a long response time or have reduced, relatively low sensitivity. New sensor platforms that can improve the response time or sensitivity, as well as other sensing characteristics, are then needed.

A radio frequency identification (RFID) tag or a planar inductor has the opportunity to provide a new sensor platform that could fulfill the need for improvements in response time and sensitivity. RFID tags consist of an antenna (i.e. planar inductor) with a microchip placed at the end of the antenna. There are three types of RFID tags: active, semi-active, and passive. Active and semi-active tags implement a battery to power the microchip. A passive RFID tag does not use a battery. Rather, a passive tag is powered through an external electric field that is coupled with the antenna. The energy transferred to the tag is used to turn the chip on, releasing the identification number encoded on the chip [1]. This information is sent back to the external source, identified as the RFID reader. By implementing an RFID sensor into a full RFID system, including the tag and external reader, one has the potential to have a wireless sensor, adding further improvements over current liquid-phase chemical sensors.

RFID tags were initially used for wireless tracking of goods and key lock systems. As RFID tags have become mainstream devices, new applications of RFID have been investigated, including the use of RFID tags as sensors in the gas phase. RFID tags are often used as sensor platforms for different applications, ranging from humidity sensing to temperature sensing to food monitoring [2,3,4]. However, in many of these applications, RFID tags are merely used as communication devices for the external sensor.

Some applications have used RFID tags as sensors in gas-phase environments [5,6,7,8] to monitor humidity and chemicals in a way that implements the sensor into the antenna coil, a planar inductor. However, very little work has been done to use RFID tags as sensors in the liquid phase. This work will focus on the use of a RFID tag as a chemical sensor in the liquid phase. A brief overview of chemical sensors, specifically RFID chemical sensors, is presented in the following sections.

1.2 Overview of Chemical Sensors

A sensor is defined as a type of transducer that receives and responds to a stimulus [9], specifically turning one form of energy into electrical energy. When detecting a signal, or measurand, the sensor produces a measureable output, typically a voltage or current that is related to the measurand. Additional signal conditioning units are often included inside the sensor system to amplify any weak electrical signals into detectable quantities for further use.

When considering the types of the measurands, sensors are classified as either physical or chemical sensors; for physical sensors, the measurand is a physical quantity, such as velocity, acceleration, force, humidity, etc whereas for chemical sensors, the measurand has chemical attributes, such as concentration of a certain chemical.

A chemical sensor can then be defined as a device that responds to stimuli produced by various chemicals or chemical reactions, converting this response to an electrical signal [9,10,11,12,13]. The sensor system consists of a device (sensor platform), a partially selective layer (molecular film), and a data acquisition system. Chemical sensors are designed to detect substances in both liquid and gaseous phases. These are used in industry, medicine, environmental monitoring, and in the military.

It is important to focus on the characteristics that define the response a chemical sensor provides due to a certain chemical and its concentration. Many different characteristics define chemical sensors, including sensitivity, selectivity, and response time. Sensitivity describes the minimal concentrations and change in the concentration (resolution) that can be successfully and repeatedly detected by the sensor [9]. This is also seen as the ratio of the change in output to the change in the value of the measurand [11,12]. Selectivity describes the degree to which a sensor responds to the desired stimulus with minimal interference from other species [10,11]. Selectivity is often used to show how a sensor responds differently to different measurands. Specifically, for chemical sensors, selectivity depends on the molecular size, shape, or polar properties of the measurand in respect to that of the partially selective film [13]. Response time is defined as how long it takes a sensor to reach 90% of its steady state value after introduction of a given concentration of the measurand [10]. Combining the different sensor characteristics will allow for proper quantification and analysis of the chemicals detected by the sensor.

A chemical sensor may be identified as either a direct or indirect sensor depending on the physical indicators that are used in the system. In direct chemical sensors, the interaction of the chemicals with the sensing material directly changes a measureable physical quantity such as resistance, potential or current. Direct chemical sensors require no further transducers as the result of the sensing is already an electrical signal. However, indirect chemical sensors utilize chemical interactions that do not result in an electrical signal. Therefore, a transducer is necessary for an indirect chemical sensor. Different types of interactions that occur in indirect chemical sensors include mass change, temperature change, change of physical shape, and frequency shifting.

There are many different sensor technologies that can be used to implement chemical sensors. These include MEMS (Micro-electrical and Mechanical Sensors), acoustic wave technology, electromagnetic technology, optical technology, and electrochemical technology. All these platforms operate under the same principle whereas the chemical interaction between the sensing layer and the target species (analyte) produces a measureable change in the state of the sensor system. RFID chemical sensors also produce measureable changes in the resistance and the resonant frequency, and represent a new class of chemical sensor platforms. In the next section the RFID Chemical Sensor, the focus of this thesis, is discussed.

1.3 RFID Chemical Sensor

RFID (Radio Frequency Identification) is a technology that allows for wireless transmission of data in a system, defined by a combination of a reader and a tag. Figure 1.1 shows the full RFID system in a simple model that details the antenna of the reader and the equivalent circuit of the tag [14]. The reader emits an electromagnetic signal at a frequency to which the tag is designed to respond. When recognizing the inquiry signal from the reader, the tag responds with the data stored on a microchip. Tags are classified into three different types: active, semi-active, and passive. The most abundant type of tag is the passive tag due to the fact that they have a low cost of production and are easily designed. Depending on the distance between the tag and the reader, the tag will either couple in the near field or the far field. If coupling in the near field, the reader and the tag are assumed to inductively couple, powering the tag through this process.

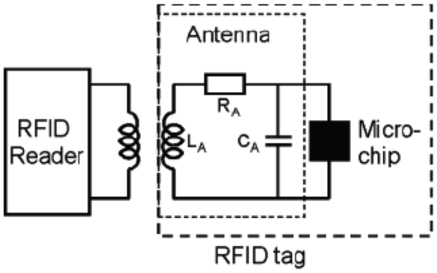

Figure 1.1 RFID system containing reader and tag

RFID tags consist of an antenna (i.e. a planar inductor coil) and a microchip, allowing them to be modeled as simple electric circuit elements, as seen in Figure 1.2. RFID tags can be considered as a planar inductor on a substrate, which can then be modeled as a parallel RLC circuit with R, the resistance of the metal traces; L, the inductance of the coil on the tag; and C, the capacitance between the coil traces [14].

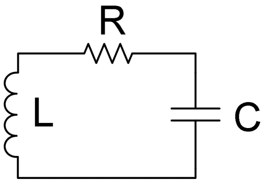

Figure 1.2 Equivalent Circuit of RFID Tag

Tags are constructed so that the R, L, and C values created by the geometry of the metal traces as well as the material properties of the substrate resonate at a specific frequency. Properly modeling the tag as basic circuit elements will aid in the analysis of the tag as a sensor since these are the components that will most likely be affected.

Many applications of RFID tags as sensors do not use RFID as the sensor platform; rather, these systems connect the RFID tag to a separate sensor, using the wireless capability of RFID to transmit the sensor signal [15,16]. The use of RFID in sensing systems provides great advantages; however, further integration of the sensing unit into the RFID tag itself would create a viable new sensor platform. There have been sensors implemented using a simple antenna to detect humidity and chemicals [5,6,7,8], but these have been only in the gas phase. Investigation of RFID chemical sensors in liquid environments is needed.

The use of RFID tags as a chemical sensing platform is relatively recent [8]. To transform an RFID tag into a chemical sensor, a chemically sensitive polymer layer must be placed on top of the tag. This analyte interacts with the polymer, causing a change in the permittivity and resistivity of the polymer. It must be noted that the changes will be seen in the parasitic capacitance, as well as the resistance of the tag. The reactive capacitance is a very small value when compared to the impedance due to the material properties of the tag. Changes to this small value of the reactive capacitance are sometimes very difficult to measure when considered in the overall impedance (hundredths of an ohm or smaller). The changes that occur in the resistance are on the same scale as the impedance due to the material properties, making them easier to measure. Changes in the resistance will be the focus of the measurements.

Changes in the polymer layer due to chemical interaction will correlate to changes in the characteristic impedance of the RFID tag. Changes in the impedance also affect the resonant frequency of the tag. The choice in polymer layer on the tag must be one that ensures the tag's resonant frequency remains in an allowable bandwidth for the tag to be read by a given external reader. If the tag's resonant frequency shifts outside of this bandwidth, it will be unable to be read by the reader.

The type of polymer coated on the surface of the RFID tag will also greatly affect the sensitivity of the RFID chemical sensor. The use of a non-conductive polymer produces a relatively small sensor response, difficult to measure since the polymer only acts as a dielectric material that affects the parasitic capacitance. In order to optimize the sensor response, we have found that the use of a conductive polymer provides a strong response. A conductive polymer will in effect short out the traces as detection occurs, providing a high level of sensitivity. A conductive polymer is ideal to enhance the sensor response. However, this polymer should not affect the response of the impedance or frequency of the tag when no chemicals are present. Many different conductive polymers can change their characteristics depending on the properties of the liquid that interacts with the polymer. One of the properties that can affect the conductivity of a conductive polymer is the pH of the liquid interacting with the polymer [17].

The problem statement will be discussed next, detailing the work that will be done to design and test a RFID chemical sensor.

1.4 Problem Statement

Previous applications of RFID Tags as chemical sensors have only involved gas-phase detection [8], with no testing conducted in the liquid phase. Present challenges of the use of a RFID chemical sensor in liquid phase include the interaction of the RFID tag with a reader. However, the feasibility a RFID liquid-phase chemical sensor could still be demonstrated.

Using a modified circuit model of an RFID tag, the resonant frequency, the sensitivity, and the quality factor will be analytically characterized for a tag coated with a chemically-sensitive film. This characterization will be used to properly identify the elements that have the greatest effect on the changes in the response of the RFID tag. Analytical equations will be obtained to provide a baseline for comparison to experimental data. Experiments will include liquid-phase testing of chemically-sensitive coated RFID tags, providing information such as changes in resonant frequency and impedance. Commercially available tags will be used for the experiments. A partially selective layer will be coated onto the RFID tag to create a chemical sensor. The sensitive layer, consisting of a layer of poly(epichlorohydrin) (PECH) followed by a layer of polyaniline (PANi), will be used to detect chemicals such as toluene and ethylbenzene. Experiments will involve the bare RFID tag to serve as a baseline for comparison to the coated tag. With the thickness of the coating kept constant, the pH of the analyte and reference solution will be varied to show different conductivity levels of polyaniline and the interaction of the conductive polymer to the RFID tag. The concentration of the chemicals will also be varied to show increased sensitivity for higher concentrations of chemicals. The end objective of this work is to create a RFID liquid-phase chemical sensor with good sensitivity, response time, and limit of detection.

1.5 Thesis Organization

This thesis is made up of five chapters. Chapter 1 gives a brief introduction to chemical sensors, their classification, and definitions for basic relevant sensor technology. Also included is a background to the RFID chemical sensor, followed by the problem statement for this work. In Chapter 2, the theory of the coated RFID chemical sensor is examined. Equations are derived to describe the theory behind the changes seen in resonant frequency and which circuit parameters cause the largest amount of change. Chapter 3 contains a brief description of the physical and chemical properties of the analytes and polymers used in this research. A description of the experimental setup and procedures are given. Chapter 4 presents the results and analysis. Sample sensor responses for the different baseline solutions are first presented followed by a comparison of the responses to the different analytes. A comparison of the measured results to the concentration of analyte is shown. Also, the limit of detection and response time for the current measurements is determined. Chapter 5 gives a summary of the findings from this research followed by possible extensions to this work.

2 RFID AS A SENSOR PLATFORM

2.1 Introduction

As described in Chapter 1, an RFID system consists of a tag and an external reader. A reader is a combination of an antenna and circuitry that outputs an inquiry signal within a specific frequency range. When used in an RFID system, the tag is tuned to resonate at the operating frequency of the reader. Many RFID systems are designed for near field operation in which inductive coupling provides the means of energy transfer between the tag antenna and the reader antenna. In this thesis, near field coupling is assumed for analysis and, while energy transfer is important, the focus of this work is to develop a chemical sensor using the RFID tag; therefore, all analysis will consist of the equivalent circuit of the tag to model operation of the sensor. When integrated into a full RFID system, the tag's impedance is reflected onto the reader for measurement. The changes seen in the reflected impedance can be correlated to the chemical analyte being detected.

The use of RFID tags as chemical sensors has been widely reported for gas-phase sensing. However, no liquid-phase application has been reported. Moreover, the reported literature for gas-phase sensing does not include detailed theory on the operating principles. It is therefore necessary to properly model the sensor system to accurately describe the measured sensor response. As stated in Chapter 1, an RFID tag can simply be modeled as a planar inductor whose equivalent circuit consists of an inductor, a resistor, and a capacitor, as shown in

Figure 1.2. Each of these elements depends on the material properties and the geometry of the RFID tag. The resistance depends on the resistivity of the metal traces of the antenna, as well as the geometry of the tag itself. The inductance depends on the permeability and geometry of the coil. The capacitance depends on the dielectric constant of the substrate and the distance between the turns of the coil. Generally, RFID tags are designed to have an additional tuning capacitor added to the system to bring the tag to the desired resonant frequency of operation. Additional circuit elements are also often seen in other models to account for lossy substrates.

2.2 Modeling of a RFID Tag / Planar Inductor as a Chemical Sensor Platform

An RFID tag chemical sensor platform consists of the RFID tag, with an external reader that generates a field to excite the tag. Current analysis and testing focuses on the planar inductor portion of the RFID tag as the chemical sensing platform. A chemically sensitive polymer film is deposited over the traces to act as the sensing layer.

As stated earlier, this concept has already been tested as a gas-phase sensor [8]. The deposition of the film perturbs the RLC circuit due to changes in the electrical properties of the polymer. The resulting modified circuit is shown in Figure 2.1. The elements added to the equivalent circuit of Figure 2.1 are the resistance of the film, $\mathbf{R_{film}}$, the change in capacitance due to the polymer coating over the turns of the antenna, $\mathbf{C_{film}}$, and the resistance associated with the distributed capacitance of the antenna windings, $\mathbf{R_{cap}}$. $\mathbf{R_{film}}$ and $\mathbf{C_{film}}$ are added due to the deposition of a polymer layer onto the antenna, while **R$_{cap}$** is associated with the distributed parasitic capacitance throughout the coil.

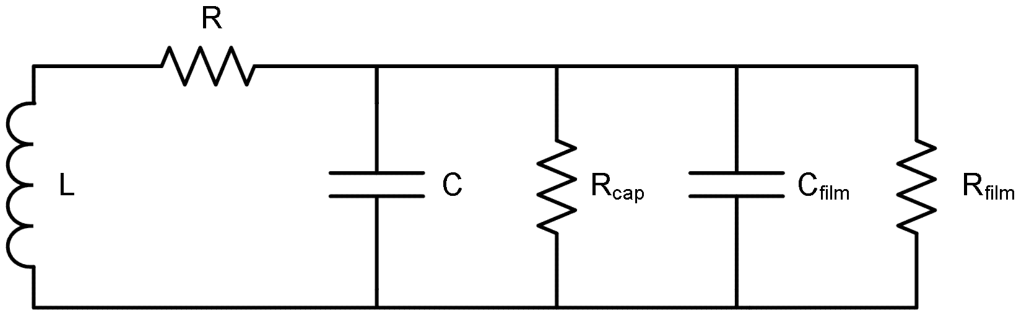

Figure 2.1 Modified RFID circuit of the coated tag

The addition of a polymer layer over a tag causes a shift in the resonant frequency of the tag. The circuit of Figure 2.1 can be further simplified to give the circuit in Figure 2.2. In Figure 2.2, the resistance of the antenna is **R$_1$**, the combined resistance of the distributed capacitance and the resistance of the film is **R$_2$**, and the combined capacitance of the antenna and the film is **C$_T$**.

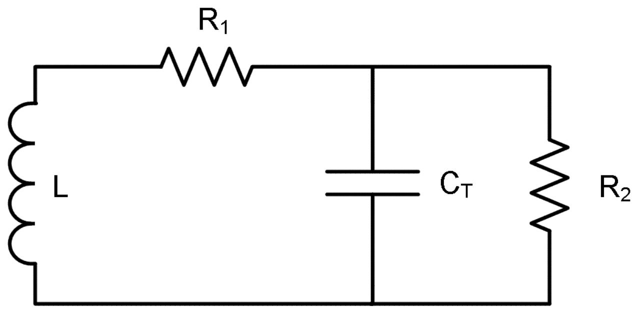

Figure 2.2 RFID equivalent circuit

The inductance of the antenna, **L** in the circuit model, is affected by the polymer layer only if the polymer is conductive. As the polymer becomes more conductive, a uniform potential is created across the tag, "eliminating" or shorting out the spaces between the traces. Without this spacing, the tag impedance exhibits behavior similar to that of a single large coil or a single sheet of metal film, reducing the inductance. The conductive polymer also causes a decrease in the capacitance for the same reason, by eliminating the gaps between the traces. When this occurs, the antenna starts to behave like a resistor.

2.3 Sensing Principles

It is desired to use the polymer coated RFID tag as a chemical sensor in liquid phase environments. The liquid layer in contact with the tag acts as a transport medium for the target chemical species. The interaction of the analyte with the polymer changes the characteristics of the polymer as sorption of the analyte occurs. The changes will be reflected in the different electrical properties of the polymer, including its resistivity and permittivity. These changes in the polymer properties will, in turn, affect both the resonant frequency and complex impedance of the tag.

The resonant frequency and the magnitude of the real component of the impedance at the resonant frequency (i.e. the resistance of the tag) are the main parameters that will be affected by the analyte sorption into the polymer due to the change in the polymer's resistivity and permittivity. Shifts in either the frequency or resistance can be correlated to the concentration of analyte is detected by the sensor. The resonant frequency of a bare RFID tag is determined from the inductance and capacitance of the coil and given by

$$\omega_o = \sqrt{\frac{1}{LC}} \tag{2.1}$$

where **L** is the inductance and **C** is the capacitance of the bare tag. The resonant frequency is often also called the center or zero-crossing frequency because this is the frequency at which the phase of the circuit is zero. When the circuit undergoes resonance, the resistance is the only non-zero portion of the impedance, as the net inductive and capacitive reactance is reduced to zero.

As previously described, a conductive polymer will effectively short out the traces as the conductivity increases. To properly understand the effect of shorting the traces out, it is necessary to understand the relationship between the geometry of the coil and the circuit elements of the planar inductor model. For a spiral planar inductor, the resistance, **R**, is given by [18,19]

$$R = \frac{1.5\,\pi\,n\,a\,R_S}{w} = \frac{\rho\,l}{w\,t_{eff}} \qquad (2.2)$$

where **n** is the number of turns, **a** is the mean radius of the coil, $\mathbf{R_s}$ is the sheet resistance of the trace (Ω/square), **w** is the width of the trace, **ρ** is the resistivity of the wire, **l** is the length of the wire, and $\mathbf{t_{eff}}$ is defined by $t_{eff} = \delta\left(1 - e^{-\frac{t}{\delta}}\right)$, where **δ** is the skin depth of the conductor and **t** is the thickness of the trace.

For the same planar inductor, the inductance, **L**, is given by [20]

$$L = \frac{d^2 n^2}{l + 0.45d} \qquad (2.3)$$

where **n** is the number of turns, **d** is the diameter of the coil in meters, and **l** is the length of the wire in meters. As the conductivity of the polymer increases and the traces begin to effectively short out, the number of turns and width of the trace will change. From Equation 2.2, it is determined that the resistance will change as a function of both the decrease in the number of turns and the increase in the width of the trace. From Equation 2.3, it is determined that the inductance will change as a function of the decrease in the number of turns, as well as the change in the length of the coil. The effective change in the number of turns and width of the trace will also cause drastic shifts in the capacitance due to the change in the geometry of the coil.

2.4 RFID Chemical Sensor: Theory

The model of the coated RFID tag is analyzed to quantify measurable parameters that will explain the changes in resistance and resonant frequency due to chemical sorption into the polymer. The parameters needed for the analysis are the resonant frequency and the relative change in frequency.

2.4.1 Resonant Frequency

Starting with the equivalent circuit of the polymer coated device (Figure 2.2), the circuit elements are combined using basic circuit analysis. The circuit is terminated from the side of the inductor since the impedance seen by the reader will be reflected from this side of the circuit. The resulting circuit analysis provides the equivalent complex impedance of the planar inductor as

$$Z_{equivalent} = \frac{R_1 R_2 + j\omega L R_2}{R_2 + (R_1 + j\omega L)(1 + j\omega R_2 C_T)} \,. \qquad (2.4)$$

The denominator of Equation (2.4) is expanded and multiplied by the complex conjugate of the denominator to determine the resonant frequency. The numerator of the relationship previously described is given by

$$Z_{num} = R_1{R_2}^2 + j\omega L{R_2}^2 - \omega^2 LR_1{R_2}^2C_T - j\omega^3L^2{R_2}^2C_T - j\omega{R_1}^2{R_2}^2C_T + \omega^2LR_1{R_2}^2C_T. \quad (2.5)$$

The resonant frequency can then be determined after modifying Equation 2.5 since it is known that resonance occurs when the imaginary portion of the impedance equals zero. This process results in

$$\omega^2L^2{R_2}^2C_T - \left(L{R_2}^2 - {R_1}^2{R_2}^2C_T\right) = 0. \quad (2.6)$$

Equation 2.6 is solved for ω, resulting in the resonant frequency of a coated RFID tag / planar inductor as

$$\omega_o = \sqrt{\frac{1}{LC_T} - \frac{{R_1}^2}{L^2}}. \quad (2.7)$$

It should be noted that the combined resistance from the polymer and the capacitance, $\mathbf{R_2}$, does not affect the resonant frequency of the planar inductor. Therefore, all changes in the resonant frequency upon sensing are functions of the change in the permittivity and resistivity of the polymer layer as they affect the geometry of the coil.

2.4.2 Relative Change in Frequency

To obtain the relative change in frequency $\left(\frac{\Delta\omega_o}{\omega_o}\right)$ for a RFID tag / planar inductor chemical sensor, it is assumed that

$$\Delta\omega_o = {\omega_o}' - \omega_o \tag{2.8}$$

where ${\omega_o}'$ is the perturbed frequency. Multiplying both sides of Equation 2.8 by $({\omega_o}' + \omega_o)$ and assuming ${\omega_o}' + \omega_o \approx 2\omega_o$ results in the following

$$\Delta\omega_o\,(2\omega_o) = {\omega_o}'^2 - {\omega_o}^2. \tag{2.9}$$

From Equation 2.9, the relative change in frequency, $\frac{\Delta\omega_o}{\omega_o}$ can be written as

$$\frac{\Delta\omega_o}{\omega_o} = \frac{{\omega_o}'^2 - {\omega_o}^2}{2{\omega_o}^2}. \tag{2.10}$$

The perturbed circuit elements are written as

$$L' = L + \Delta L \tag{2.11a}$$
$${C_T}' = C_T + \Delta C_T \tag{2.11b}$$
$${R_1}' = R_1 + \Delta R_1. \tag{2.11c}$$

${\omega_o}'$ is given by

$${\omega_o}' = \sqrt{\frac{1}{L'{C_T}'} - \frac{{R_1}'^2}{L'^2}}. \tag{2.12}$$

Substitution of Equation 2.7 and Equation 2.12 into Equation 2.10 gives

$$\frac{\Delta\omega_o}{\omega_o} = \frac{\left(\frac{1}{2}\left[\frac{1}{L'{C_T}'} - \frac{{R_1}'^2}{L'^2}\right]\right) - \left(\left(\frac{1}{2}\right)\left[\frac{1}{LC_T} - \frac{{R_1}^2}{L^2}\right]\right)}{\frac{1}{LC_T} - \frac{{R_1}^2}{L^2}}. \tag{2.13}$$

It is desired that the relative change in frequency be expressed in terms of the relative changes in the lumped element components, $\left(\frac{\Delta L}{L}\right)$, $\left(\frac{\Delta C_T}{C_T}\right)$, and $\left(\frac{\Delta R_1}{R_1}\right)$.

Further substitution of Equations 2.11(a-c) into Equation 2.13 gives the relative change in frequency as:

$$\frac{\Delta\omega_o}{\omega_o} = \frac{\left(\frac{1}{2}\left[\frac{1}{(L+\Delta L)(C_T+\Delta C_T)} - \frac{(R_1+\Delta R_1)^2}{(L+\Delta L)^2}\right]\right) - \left(\left(\frac{1}{2}\right)\left[\frac{1}{LC_T} - \frac{{R_1}^2}{L^2}\right]\right)}{\frac{1}{LC_T} - \frac{{R_1}^2}{L^2}}. \qquad (2.14)$$

Binomial expansion is applied to the terms of Equation 2.14 assuming that the changes in the values are small and that the responses are all first order effects, resulting in

$$\frac{1}{(L+\Delta L)(C_T+\Delta C_T)} = \frac{1}{LC_T}\left(1 - \frac{\Delta L}{L} - \frac{\Delta C_T}{C_T}\right) \qquad (2.15a)$$

$$\frac{(R_1+\Delta R_1)^2}{(L+\Delta L)^2} = \frac{{R_1}^2}{L^2}\frac{\left(1+\frac{\Delta R_1}{R_1}\right)^2}{\left(1+\frac{\Delta L}{L}\right)^2} = \frac{{R_1}^2}{L^2}\left(1 + 2\frac{\Delta R_1}{R_1} - 2\frac{\Delta L}{L}\right). \qquad (2.15b)$$

Substituting Equations 2.15(a-b) into Equation 2.14 and rearranging in terms of $\left(\frac{\Delta L}{L}\right)$, $\left(\frac{\Delta C_T}{C_T}\right)$, and $\left(\frac{\Delta R_1}{R_1}\right)$, results in the relative change in frequency of a coated RFID tag / planar inductor as:

$$\frac{\Delta\omega_o}{\omega_o} = \frac{\Delta L}{L}\left(\frac{-\left(2{R_1}^2C_T-2L\right)-L}{2{R_1}^2C_T-2L}\right) + \frac{\Delta C_T}{C_T}\left(\frac{L}{2{R_1}^2C_T-2L}\right) + \frac{\Delta R_1}{R_1}\left(\frac{2{R_1}^2C_T}{2{R_1}^2C_T-2L}\right) \qquad (2.16)$$

This equation is helpful to predict which of the components will have the largest effect on the sensitivity of the sensor.

2.5 RFID / Planar Inductor as a Sensor Platform in Liquid

2.5.1 RFID Operation in Liquid

RFID tags as currently designed would not work well in liquid [21]. The introduction of dielectric spacers would be required to decrease the parasitic capacitance and allow for use in a fluid. However, other researchers were able to read a tag through a liquid medium, although the liquid was not interacting with the surface of the tag [22]. These experiments show that RFID communication through a liquid is feasible, but dependent on the reader. Since the focus of this work is the RFID tag / planar inductor chemical sensor, the most important factor to consider is the effect that the liquid has on the electric field.

As a liquid flows over the surface of a RFID tag, as indicated in Figure 2.3, the liquid will inhibit the ability of the tag to couple to an external energy source due to the changed dielectric that is in the fluid. This reduction in external energy will lead to an increase in loss, seen in the resistance, and a shift in the resonant frequency due to the decrease in parasitic capacitance from the dielectric constant changing from air to that of the liquid.

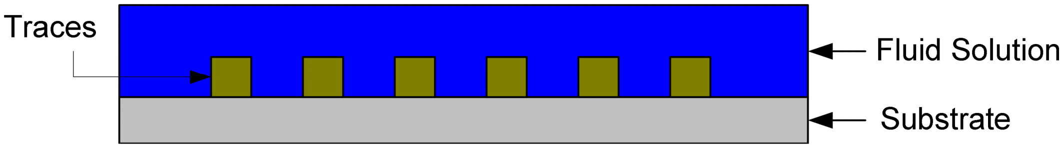

Figure 2.3 Bare RFID tag in liquid

An example of the changes expected in the response of the tag is illustrated in Figure 2.4. These changes include a decrease in both the resistance and the resonant (or center) frequency. While liquids have a large effect on RFID tags, the effect is reduced when a polymer layer is introduced on top of the antenna. This change in resistance and resonant frequency occurs because the polymer layer traps the electric field, thus allowing less energy to be lost into the liquid.

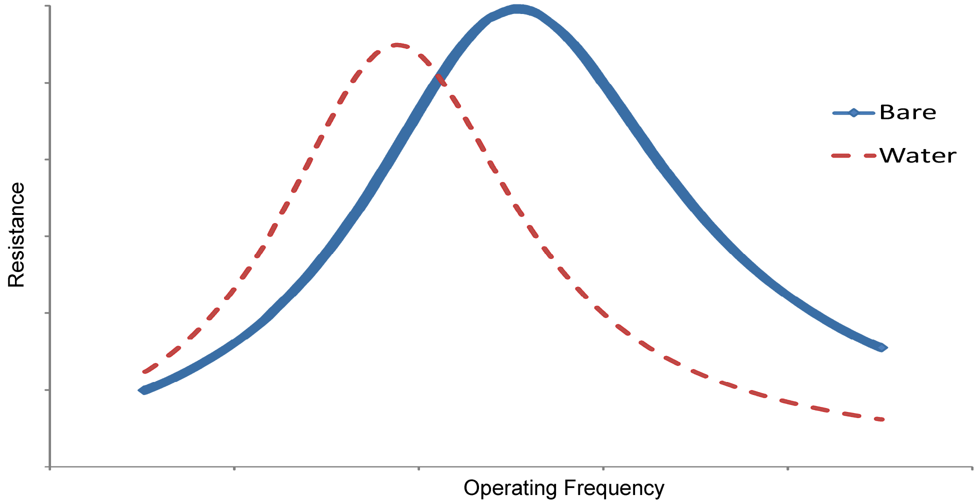

Figure 2.4 Comparison of bare tag response to response of coated tag in liquid

2.5.2 Effects of Coated RFID Tag / Planar Inductor in Liquid

For chemical sensing applications, a polymer layer is deposited on the traces. In the present study, polyepicholorhydrin (PECH), will be used as the base layer in the RFID tag chemical sensor. A diagram of this configuration is shown in Figure 2.5. This polymer layer isolates the electric field from the fluid. However, for this to be most effective, a very thick polymer layer is necessary.

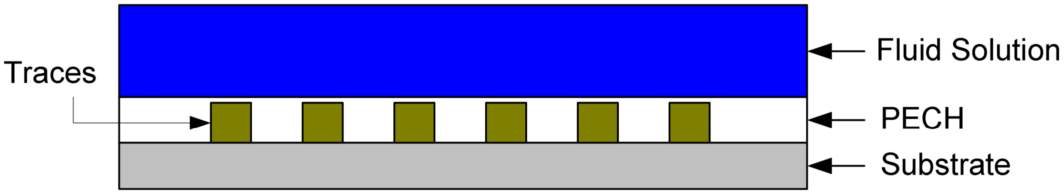

Figure 2.5 RFID Tag Coated with a Polymer in liquid

Although the use of a very thick polymer layer is the most effective way to ensure that the liquid is isolated from the charge in the traces, it does not contribute to ensure the highest sensitivity. Previous work by Marioli, et al. [23] shows that an ideal polymer layer does not completely cover the traces. This technique isolates the electric field to ensure that the RFID tag works as designed.

In general, a chemically sensitive polymer film is selected for the detection of a particular analyte. For the detection of analytes in liquid environments, the analyte must displace the liquid's molecules from the area near the coating surface and in the coating. The interaction between the analyte and the polymer layer will result in changes to the physical properties of the polymer. A single polymer layer of PECH over an RFID tag will allow for changes in the parasitic capacitance due to changes in the dielectric constant of the film as a result of analyte sorption. Because PECH has a low conductivity, it has minimal effects on the resistance associated with the traces of the RFID tag. The introduction of a chemically sensitive conductive polymer could allow for higher sensitivity as detection occurs due to the changes to the geometry of the coil that would occur.

2.5.3 Effects of RFID Tag / Planar Inductor Coated with a Conductive Polymer in Liquid

A conductive polymer will affect the response of the coil by connecting the traces of the tag, effectively shorting out the traces to act like a single metal sheet. There are many different types of conductive polymers, including some that are conductive and others that become conductive as they interact with the solutions or the analytes. Polyaniline (PANi), a conductive polymer, is used in the present work. Because PANi cannot adhere to any medium, including the bare RFID tag / planar inductor, a layer of PECH was utilized as both as a sensing layer as well as the base layer onto which the PANi layer could be deposited. The multi-layer sensor is illustrated in Figure 2.6.

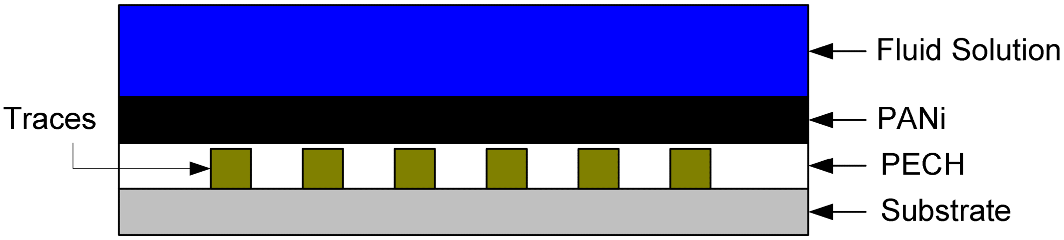

Figure 2.6 RFID tag coated with a conductive polymer in liquid

Addition of PANi to the sensor configuration will allow for increased sensitivity over a single layer of PECH. This increased sensitivity occurs because the conductive polymer will change the geometry of the coil, affecting the values of resistance and resonant frequency more than that of a single layer of PECH. Therefore, the multi-layer sensor configuration is implemented for this work.

3 EXPERIMENTAL METHODS

3.1 Introduction

The objective of this research is to investigate the applicability of an RFID sensor as a chemical sensor in liquid phase. To test this concept, a dual layer sensor system consisting of poly(epichlorhydrin) (PECH) and polyaniline (PANi) as the partially selective polymers will be investigated for detection of toluene and ethylbenzene. The sensor is characterized through experiments that are designed to test the sensitivity and selectivity of the sensor when subjected to the different analytes. The experiments consist of exposing the RFID sensor to combinations of baseline solutions with different pH values and the different analytes. The experiments are performed several times to confirm that the results are repeatable and reproducible. In designing the experimental setup, efforts were taken to minimize the noise in the system that would affect the measured response (i.e. the resonant frequency and complex impedance) of the sensor. The experiments consist of first exposing the sensor to a reference solution, and then allowing for the system to stabilize. Upon system stabilization, the sensor is exposed to the analyte solution and then allowed to reach equilibrium. The analyte next is flushed from the system using the reference solution. This process is repeated for increasing concentrations. A typical set of data is shown in Figure 3.1, measuring the resistance of the sensor for varying concentrations of the analyte. This data is representative of that measured throughout the different experiments. Similar data is obtained for the monitoring of the resonant frequency of the sensor.

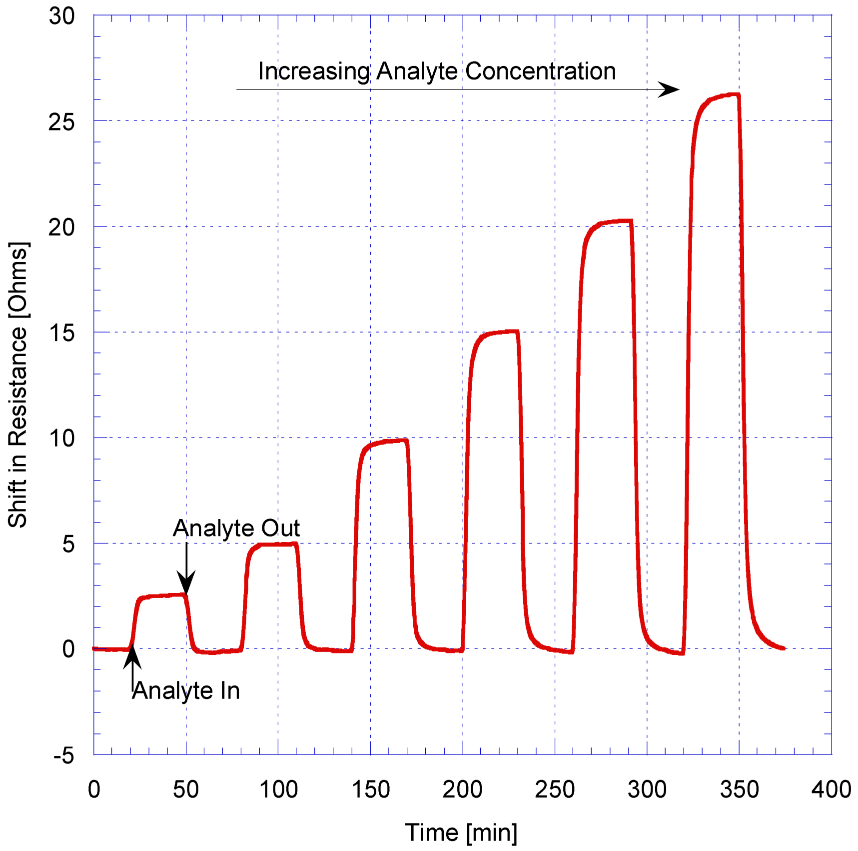

Figure 3.1 Representative data for the experiments performed. This data monitors the change in resistance as the concentration of analyte is increased over time.

Section 3.2 describes the materials and apparatus used in this set of experiments, as well as the steps taken in preparing the baseline, analyte, and polymer solutions and preparing the device for coating and experimentation. Section 3.3 details the equipment setup and procedures used for coating the device and collecting data.

3.2 Apparatus and Materials

All analytical-grade materials used in this research were purchased from Sigma-Aldrich (Milwaukee, WI) and used as supplied.

3.2.1 Baseline Solution and Preparation

It is known that PANi becomes more conductive when in the presence of a strong acid [25,26,30,31]. Therefore, it is important to prepare acidic solutions to be used as the baseline solution and as the carrier solution. HCl is diluted with de-ionized (DI) water to prepare different solutions of varying acidity, which in turn varies the conductivity of the polymer. HCl has a molecular weight of 36.46 g/mol and a density of 1.2 g/mL [32]. The pH of the solution depends on the concentration of HCl in the solution. A higher acidic solution contains a higher percent concentration of HCl.

Preparation of the baseline solution begins with proper cleaning of the required containers. DI water is added to a certain amount of HCl to prepare a solution with a desired pH. Knowing that the molecular weight of HCl is 36.46 g/mol [32], a solution that is 1 M would require 36.46 g in 1000 mL solution. Another solution of 0.001 M was prepared by adding 36.46 mg in 1000 mL. Using a pH meter [40], the solutions were measured to determine the pH, as indicated in Table 3.1.

Amount of HCl in 1000 mL Flask (g)	Molarity of Solution	pH of Solution
0.03646	0.001 M	3.5
36.46	1 M	1

Table 3.1 Data table for preparation of different baseline solutions

3.2.2 Analytes and Analyte Solution Preparation

The analytes used in these experiments are toluene and ethylbenzene. These analytes were chosen for the harmful nature that they have on humans. The EPA has set a maximum limit allowed for both of these chemicals in drinking water [42]. Individual states also have limits placed on the amount of these chemicals present in waste water. For example, for Wisconsin, the daily limits of toluene and ethylbenzene are 200 ppb and 140 ppb respectively for waste water [43]. It is necessary to have a sensor capable of detecting at least this level of chemical concentration, and ideally lower concentrations as well.

Toluene is a clear, water-insoluble liquid that is often used as industrial feedstock. Toluene has a boiling point of 111˚C, molecular mass of 92.14 g/mol, and the empirical formula of ($C_6H_5CH_3$) [27]. Ethylbenzene is a dangerous byproduct that is produced during the creation of polystyrene, a commonly used plastic material. Ethylbenzene has a boiling point of 136 ˚C, molecular mass of 106.167 g/mol, and the empirical formula of $C_6H_5C_2H_5$ [28].

Preparation of the analyte solution begins with proper cleaning of the containers. De-ionized water (DI) and 100 mL of previously described baseline solution are both added to a 1000 mL flask. A specific amount of analyte is added to create a solution with the desired concentration (ppm). The appropriate volume of analyte is determined using the expression given by

$$concentration\ in\ ppm = \frac{mass\ of\ analyte\ (g) \times 10^6}{mass\ of\ analyte, DI\ water, and\ baseline\ solution\ (g)} \tag{3.1}$$

Once the analyte is added to the mixture of DI water and baseline solution, the resulting solution is placed on a stirrer for an hour to ensure equal distribution of the analyte throughout the flask. From Equation 3.1, a solution of 1 ppm for each analyte was obtained. From the initial concentration, each analyte was then diluted to a desired lower concentration. Table 3.2 shows the required volume of the analytes ethylbenzene and toluene for these experiments.

Vol. Baseline Solution (mL)	Vol. Analyte Solution (mL)	Concentration of Toluene (ppm)
0	120	1.038000168
27	93	0.804450101
51	69	0.596850056
74	46	0.397900025
97	23	0.198950006
109	11	0.095150001

Vol. Baseline Solution (mL)	Vol. Analyte Solution (mL)	Concentration of Ethylbenzene (ppm)
0	120	1.04039969
27	93	0.806309814
51	69	0.598229897
74	46	0.398819954
97	23	0.199409989
109	11	0.095369997

Table 3.2 Data table for preparation of toluene and ethylbenzene analyte solutions

3.2.3 Polymers and Polymer Preparation

The two chemically sensitive polymers that are used are PECH and PANi. PECH has an average molecular weight of M_w=700,000 and a bulk density of 1.36 g/mL [29]. PECH is classified as a rubbery polymer at room temperature because of its low glass transition temperature of -25.5 °C [10]. The rubbery nature of PECH allows for PANi to adhere to it, while also acting as a chemically sensitive layer.

PANi has an average molecule weight of $M_w = 65{,}000$ [24]. Depending on the chemical composition of PANi, the polymer is either conductive or insulating. The form of PANi used in the present work is the emeraldine-base structure of PANi, which is insulating [24]. However, when emeraldine-base PANi comes in contact with a strong acid, it changes from an insulating polymer to a conductive polymer [25,30]. In an acidic environment, the emeraldine-base of PANi interacts with the hydrogen atoms from the acid. This process, in which the hydrogen atoms (protons) are added to the polymer chain, is referred to as protonation of the polymer. Figure 3.2 shows the chemical reaction for this process [26]. Hydrochloric acid (HCl) is an acid that has been documented to protonate PANi. When HCl interacts with PANi, the chlorine ions that bond to the nitrogen atoms in PANi cause the formation of radical cations. These radical cations in the PANi allow for increased charge mobility throughout the polymer chain, causing the change in conductivity [26]. When the acid is removed from the PANi, the polymer returns to the insulating form as the chemical reaction is reversible. Since PANi becomes conductive when protonated, it is beneficial to use an acidic solution for sensing measurements.

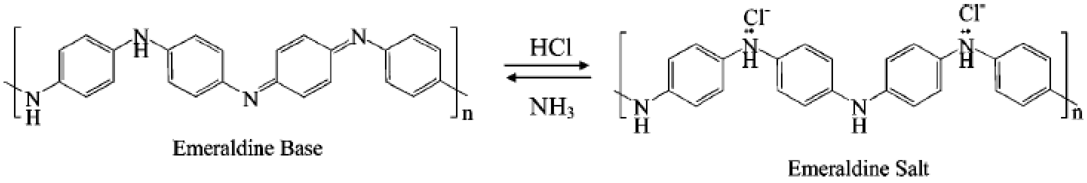

Figure 3.2 Chemical Reaction of PANi from Insulating to Conductive Form

The process in which PANi becomes increasingly conductive has been well researched. MacDiamard, et al. [31] explains how PANi reacts when exposed to varying levels of pH in a solution and is shown in Figure 3.3. PANi has three specific regions of conductivity depending on the pH of the solution: if the solution ranges from a pH of 7 to 4, the conductivity remains very low; if the solution ranges from a pH of 4 to 2, the conductivity increases in a linear fashion; and if the solution decreases from a pH of 2 to negative values, the conductivity remains constant at a high value.

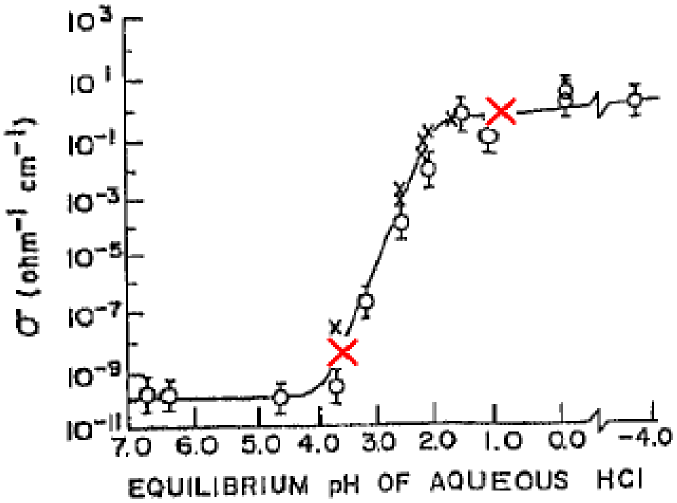

Figure 3.3 Conductivity of PANi as a function of exposure to HCl. The red marks are the pHs used in the present experiments

As the conductivity increases, the protonation of PANi causes the gaps between the traces to be shorted out. The shorting of the traces causes the capacitance to greatly decrease, with the inductance increasing as the coil begins to act like a single sheet conductor. When PANi is in its conductive form, it affects the traces in a manner that allows for higher sensitivity due to the changed geometry. This will cause a large increase in the resonant frequency of the tag and a decrease in resistance.

It should also be noted that both PECH and PANi are stable in water, a key requirement for liquid phase applications.

The polymers PECH and PANi are prepared using similar solution preparation procedures. PECH is supplied as a rubbery mass, while PANi comes in granular form. The solvents used to dissolve the polymers are chloroform and xylenes respectively for PECH and PANi. Polymer solutions are prepared by using the weight/weight definition for percent solutions given by

$$\%\, wt = \frac{mass\ of\ polymer\ (g)}{total\ mass\ of\ solution\ (g)} \times 100 \qquad (3.2)$$

The concentrations of polymer solutions prepared are 2.99% wt PECH and 2.52% wt PANi. The general procedures for preparing the polymer solution are given as follows [10]:

1. Calculate the mass of solvent and polymer needed to prepare a specific *% wt* polymer solution.
2. Clean solution container and dry.
3. Place the dried vial on an electronic balance and zero. Add polymer until desired mass is reached.
4. Using a pipette, add solvent to the container until the total mass of the polymer and the added solvent reaches the determined value for the desired *wt%* solution.

5. Seal the vial and place on a magnetic stirrer. Leave solution on stirrer for 24 hours.

This procedure has been repeatedly used in the Microsensor Research Laboratory. The difference in the procedures for PANi involves an additional 30 minutes of the solution being placed in an ultrasonic cleaner to ensure all loose particles are properly mixed [39]. This sonication occurs during the first hour of the 24 hour stirring period.

3.2.4 RFID Tags and Preparation

RFID tags were received as samples from RCD Corporation [34]. Figure 3.4 shows a tag before any preparation and after coating. On the left is a tag that is bare and is placed on a glass slide for preparation. The tag on the right is after it is coated with the dual layer film of PECH and PANi.

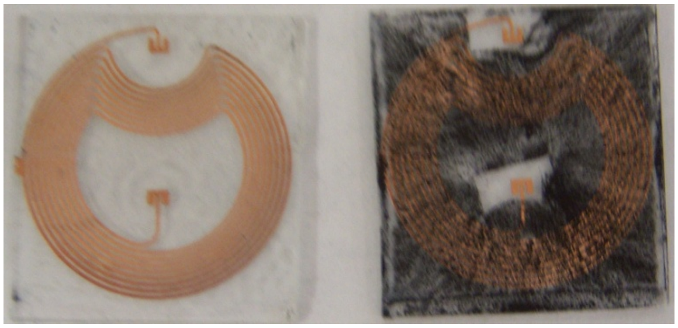

Figure 3.4 A commercial RFID tag from RCD Corporation. Model HFR11FCP8.0. A bare tag is shown on the left, with the coated tag on the right.

The tags are first tested to ensure they resonate at the designed frequency. As the tags are manufactured on thin plastic for use in many different environments, it is necessary to place them on a solid surface that will provide support for the coating process without interfering with the test results. To solve this problem, glass slides are used as substrate for the tag throughout the experimentation process. The glass slides are trimmed to the same size as the tags to ensure they will fit in the test cell. The tags are secured to the glass slide using 3M Spray Mount Artist's Adhesive [35]. The adhesive is first sprayed on the glass slide, and the tag is placed on top of the adhesive. Once the tags are placed on the glass slide, they are left to dry overnight in the dessicator before the polymer coating process.

3.2.5 Flow Cell

A specially designed flow cell was fabricated to facilitate exposure of the polymer-coated RFID tag to the aqueous solution containing the analyte. The cell was fabricated at the Discovery Learning Center at Marquette University [36]. The cell acts as a holder for the tag on the glass slide, as well as the connection point for the Vector Network Analyzer (VNA). Figure 3.5 shows the designed flow cell, and Figure 3.6 shows the fabricated flow cell. Fluid flows into the flow cell through the inlet. The fluid is directed over the RFID sensor that is placed in the middle of the flow cell. The fluid leaves the flow cell through the outlet.

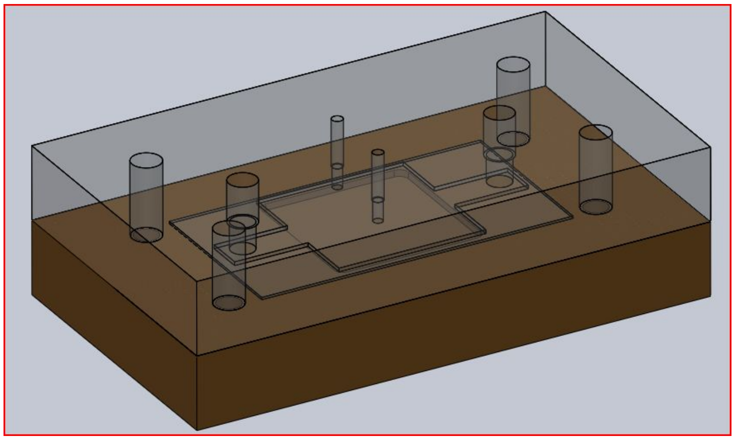

Figure 3.5 Solidworks design for RFID liquid-phase flow cell.

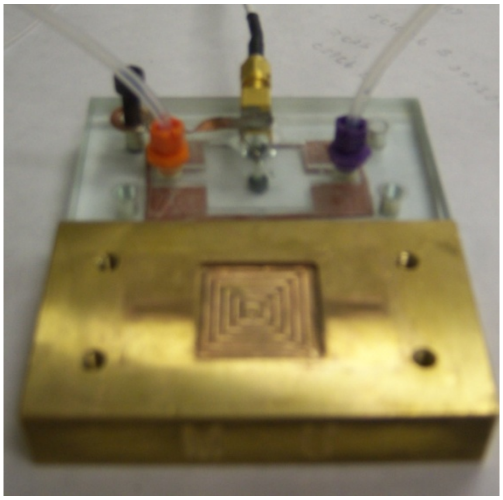

Figure 3.6 Flow cell used for device characterization and experimentation. Designed and manufactured by the Marquette University Discovery Learning Center.

The base has a recess to hold the tag. The polycarbonate top houses the pogo-pins that connect the tag to the VNA. The cell is fitted with inlet and outlet ports. A specially designed gasket fits around the flow area to provide an airtight seal for the flow system. The tubing and connectors also provide an airtight seal for the system so that the proper pressure can allow aqueous solutions to flow through the system. Gaskets around the pogo-pins shield them from the liquid.

3.2.6 Vector Network Analyzer

The Hewlett Packard HP8753C VNA is used in this experiment. The VNA includes the capability to convert S-parameter data to impedance data [38]. The feature of converting to impedance internally allows the ability to track change in the resonant frequency and in the real impedance. A computer is used to collect data every 20 seconds.

A special calibration kit was created to properly calibrate the flow cell connection to the VNA. The kit was created by modifying RFID tags placed on glass slides. A short was created by soldering a wire to each contact, with an insulator under the wire so the wire did not contact the coil (Figure 3.7). An open was created by slicing the traces near the contacts (Figure 3.8). A 50 Ω load was created by soldering a 51 Ω chip resistor to the contacts, similar to the short as previously described (Figure 3.9). Each of these calibration tags were placed in the flow cell and tightened to ensure proper connection of the pins to the contacts. When each of the tags had been used to create the entire calibration on the VNA, the resulting calibration setting was saved for further use in the present work.

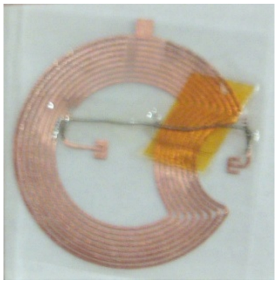

Figure 3.7 RFID Cal – Short

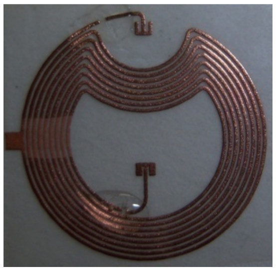

Figure 3.8 RFID Cal – Open

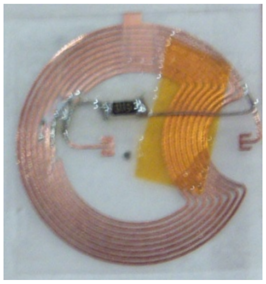

Figure 3.9 RFID Cal – 50 Ohm Load

3.3 Equipment Setup and Procedures

3.3.1 Equipment Setup

The experimental setup for this investigation consists of the VNA measurement system, the sensing system, and a liquid sample delivery system. This setup is available in the Microsensor Research Laboratory at Marquette University for liquid-phase chemical-sensor research and development. The VNA measurement system consists of the VNA and PC-based Labview control software for data acquisition. The data (real impedance and frequency) collected by the network analyzer is transmitted to the PC for data analysis.

The Specialty Coating System (SCS) Model P6700 spin coater is used in this experiment for film deposition on the RFID tag [33]. A typical spin coating process involves depositing a small volume of the polymer solution onto the center of the coil followed by spinning the device at a high speed [33]. Centripetal force causes most of the polymer solution to spread while the tag is held steady by a vacuum chuck. Any excess solution flies off the edge of the substrate, leaving behind a thin film of polymer on the tag. The final film thickness and other properties depend on the nature of the polymer solution (viscosity, drying rate, percent solids, etc.) and the spin parameters (spin speed, acceleration, and ramp time) chosen for the spinning process [33]. The vacuum holds the tags in place as they are spun at 5000 rpm. The settings used in the spin coating process can be found in Appendix A.

A peristaltic pump (Cole Parmer Model 7518-00) is used to control the flow of aqueous solutions from the vial through the cell and into a waste container. The pump was calibrated before initial use [37].

The sensing system includes the RFID tag mounted on a glass slide inside a specially designed flow-through cell to facilitate exposure of the coated device to the liquid of interest. The liquid sample delivery system consists of a peristaltic pump, a waste container, aqueous solution, and the connecting tubes. The experimental setup is shown in Figure 3.10.

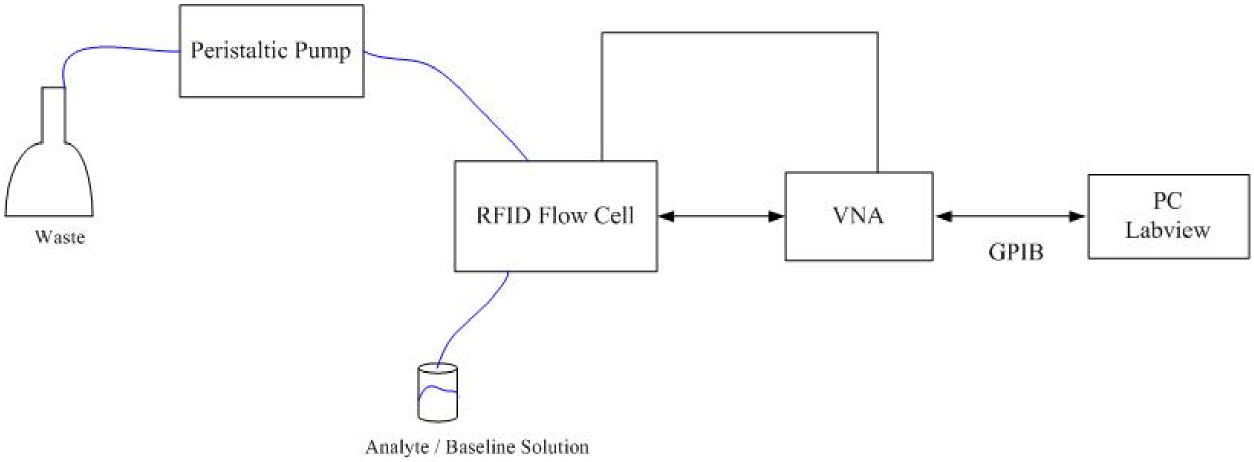

Figure 3.10 Diagram of the Experimental Setup used to measure real and reactive impedance for a RFID tag exposed to Analyte / Baseline solution

3.3.2 Procedures

To conduct an experiment, the device must first be coated with the prepared polymers. Once coated, the baseline and analyte solutions are prepared as previously described. The coated device is then subjected to the baseline and analyte solutions with the use of the flow cell while data acquisition is performed.

Device Coating

Before coating a tag, the electrical contacts are masked using Kapton tape to prevent the contacts from being coated by the polymer. The use of Kapton tape shields the contacts, ensuring proper electrical connection after coating. Once the coating process is completed, the chuck and the bottom of the device are cleaned thoroughly using cotton-tipped applicators and chloroform [10]. No chloroform or other chemicals are used on the surface of the tag as the chemicals break down the adhesive layer between the traces and the plastic backing of the tag.

In the current experiments, a layer of PECH is first coated onto the RFID tag, followed by a layer of PANi. To ensure consistency in the layers, the same spin speeds and ramp times are used for each polymer. The coatings are performed consecutively, with a cleaning of the chuck to ensure that no excess polymer affects the coating process. The coating must be uniform to create an effective sensing layer [10]. A crude form of optical verification was performed to ensure a uniform coating layer was present. The coated device was cured in ambient air for 19 hours in a desiccator to ensure no dust or any other molecules adhere to the polymer.

The final film thickness is a function of the viscosity of the polymer solution and spin coating conditions. A thickness characterization experiment was performed to determine the appropriate spin coating speed and polymer solution concentration for a desired film thickness [10]. A microbalance scale [44] was used to estimate the thickness of the polymer layer for each coated tag using the following expression

$$thickness(m) = \frac{coated\ tag\ mass\ (g) - bare\ tag\ mass\ (g)}{width\ of\ tag\ (m) \times length\ of\ tag\ (m) \times density\ of\ polymer\ \left(\frac{g}{cm^3}\right)}.$$

(3.3)

Data Acquisition and Analysis

Prior to each measurement, a full one-port calibration of the VNA is performed by following the steps outlined in [41] using the calibration kit as previously described. Once saved, the calibration file includes the settings regarding center frequency, span, and other necessary measurement settings, and is recalled before each experiment. The pump is started to fill the cell with the baseline solution. Air bubbles are removed from the cell by tapping the sides until the bubbles move to the outlet of the cell. This removal of air bubbles is necessary to avoid disturbance of the sensor response [10]. The aqueous solution is flowed over the tag at 1 mL/min to keep low pressure and allow for laminar flow over the tag.

A Labview program is started after introducing the baseline solution into the cell to continuously collect data. The data received from the Labview program, i.e. the resistance and resonant frequency, is saved for subsequent data analysis.

After stabilizing the device in the baseline solution for one hour, analyte is introduced into the flow cell. A preconditioning run of the lowest concentration in ppm is performed. Upon completion of preconditioning, the analyte solution is flushed with the baseline solution. Once it is ensured that the response has returned to the baseline after another half hour, the concentration of the analyte solution is routinely increased every half hour, flushing for another half hour between concentrations. This process is repeated until the highest concentration has been reached and flushed, at which point the experiment is complete.

Upon completion, the results are transferred for data analysis. The results will be analyzed in terms of sensitivity, selectivity, limit of detection, and response time.

4 Results and Discussion

4.1 Introduction

A coated RFID tag with a two-layer film consisting of polyaniline (PANi) over poly(epichlorhydrin) (PECH) was investigated for the detection of organic compounds (toluene and ethylbenzene) in liquid phase environments. Four different experiments were performed and repeated to ensure reproducibility. In this chapter, results from the experiments are shown and discussed by analyzing the sensor response to determine the sensitivity of the polymer layer to the different analytes. The shifts in the real part of the impedance (resistance) and resonant frequency due to analyte sorption are measured. This chapter also details the different responses of the two-layer film to the different pH baseline solutions used. A comparison of partial selectivity of the film layer is also included to show the different responses of the sensor to similar concentrations of toluene and ethylbenzene. A discussion on the limit of detection of both analytes in each baseline solution is included, as well as an analysis on the response time of the system to each analyte. The information presented here is expected to be used in the design and implementation of RFID chemical sensors in liquid phase environments.

4.2 Sensor Responses

Several different experiments were performed for different analyte / baseline solution pairs with the same film. Figures 4.1 through 4.10 show typical sensor responses (change in resistance and resonant frequency shift) to varying concentrations of toluene (0.1–1ppm) and ethylbenzene (0.1–1ppm) in aqueous solutions after it has been baseline corrected. A set of raw data is shown in Appendix B, along with details as to how the baseline correction was performed. The measured changes in resistance and resonant frequency can be correlated directly with the analyte-induced changes in the viscoelastic properties of the film layer. The pH of the solution also contributes to the different responses. As the concentration of chemical increases in the baseline solution, the pH of the baseline solution also increases, becoming more basic. This change in pH appears to further contribute to the response due to the conducting nature of PANi.

There were large spikes in the resonant frequency when using a baseline solution of pH = 1 at a concentration of 1 ppm, seen in Figures 4.2 and 4.6. These large spikes are due to the change in acidity as the pH increases as the concentration increases. A concentration of 1 ppm shifts the pH of the solution near a pH = 2, which is on the crest of the linear region. At this point, the frequency increases due to the decrease in the protonation of the polymer. There is also a large spike in the frequency in Figure 4.4. This spike is due to a decrease in the resonant frequency that quickly increased when the analyte solution was flushed with the baseline solution. The spike is due the baseline correction of the measured signal.

The RFID tag is coated with an estimated thickness of 1.5 µm total layer thickness as determined by thickness estimations performed. While the same recipe and volume of polymer was used to create the film for each tag, the thickness varied slightly. The slight difference in thickness for the same layer may be due to a small difference in temperature, therefore viscosity. Although the total film layer varies per experiment, the consistent method used to create the polymer layer allowed for reproducible data using a PECH / PANi dual layer film.

The measured shift in resistance for two identical experiments is shown in Figure 4.9 and Figure 4.10. The relative times of analyte injection and flush have been shifted for comparison of the two experiments. The large difference between the two experimental results in Figure 4.10 is due to the fact that new sets of baseline and analyte solution were prepared for each run. While similar concentrations were prepared, it could not be verified that the solutions were identical. It should also be noted that the shift in both resonant frequency and resistance was completely reversible when the analyte solution was flushed with the baseline solution.

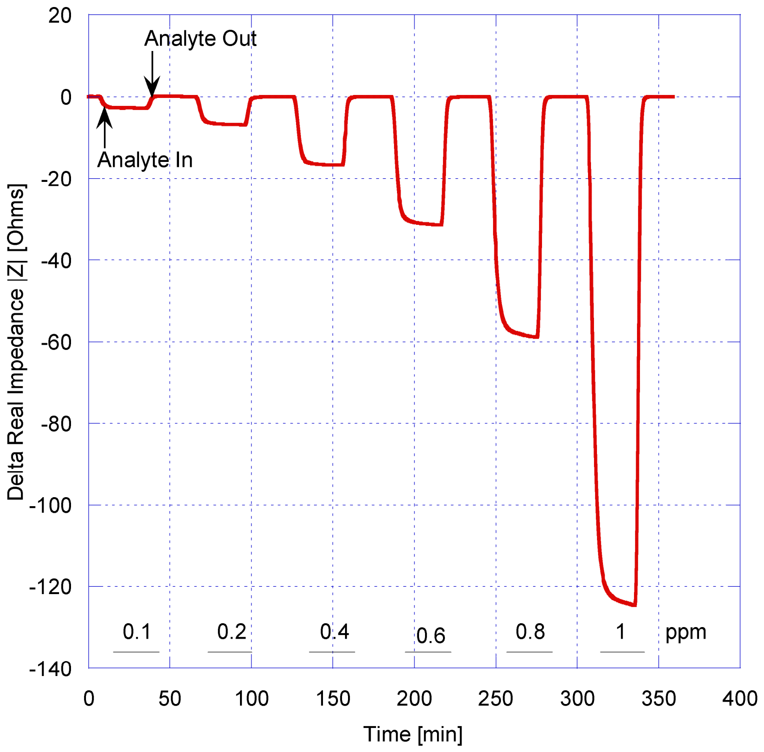

Figure 4.1 Change in Resistance of RFID Sensor to Increasing Concentration of Toluene in an Aqueous Baseline Solution of pH =1

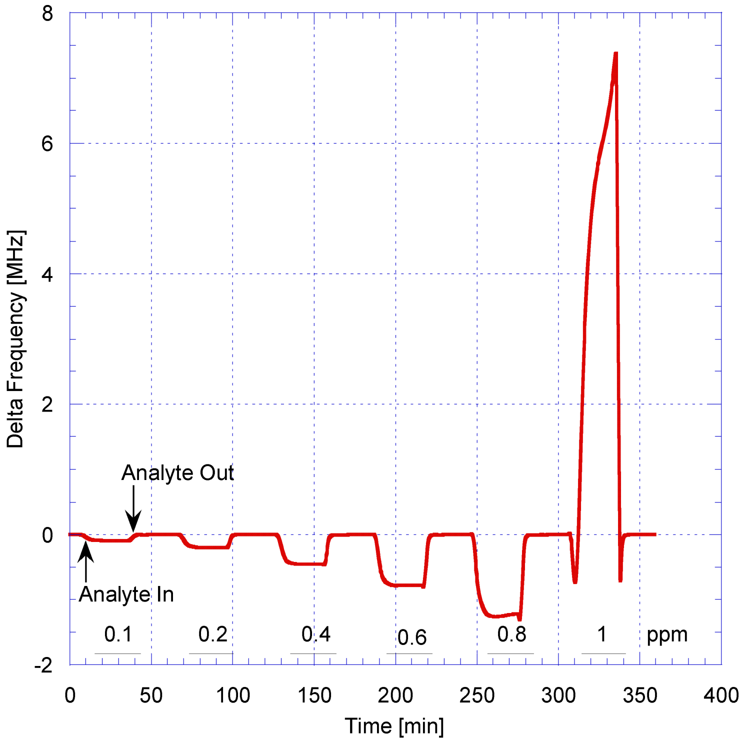

Figure 4.2 Change in Frequency of RFID Sensor to Increasing Concentration of Toluene in an Aqueous Baseline Solution of pH = 1

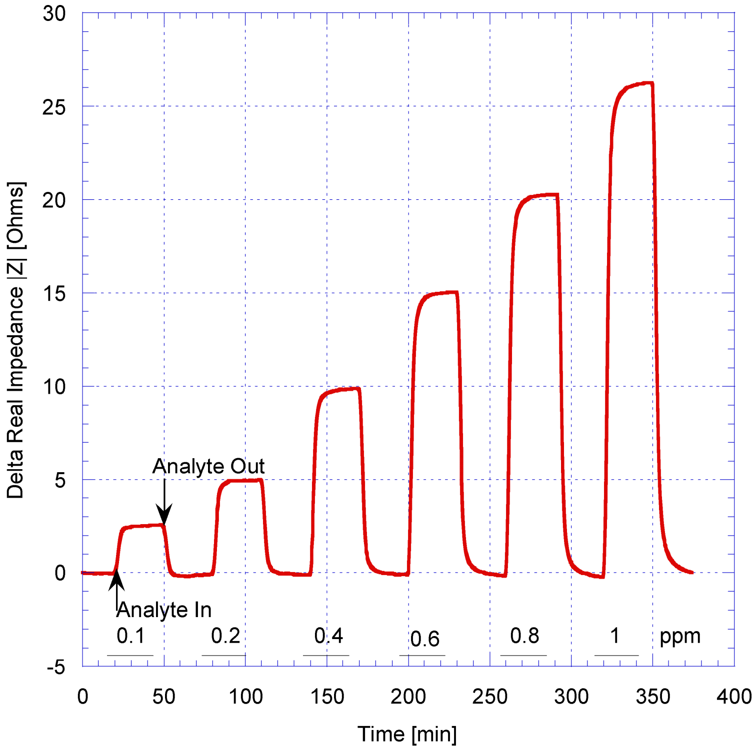

Figure 4.3 Change in Resistance of RFID Sensor to Increasing Concentration of Toluene in an Aqueous Baseline Solution of pH = 3.5

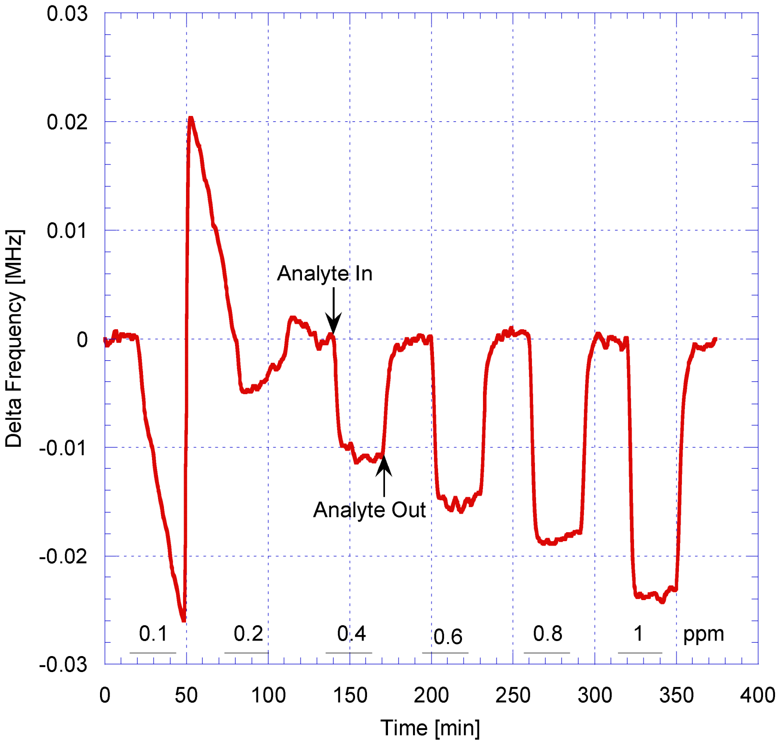

Figure 4.4 Change in Frequency of RFID Sensor to Increasing Concentration of Toluene in an Aqueous Baseline Solution of pH = 3.5

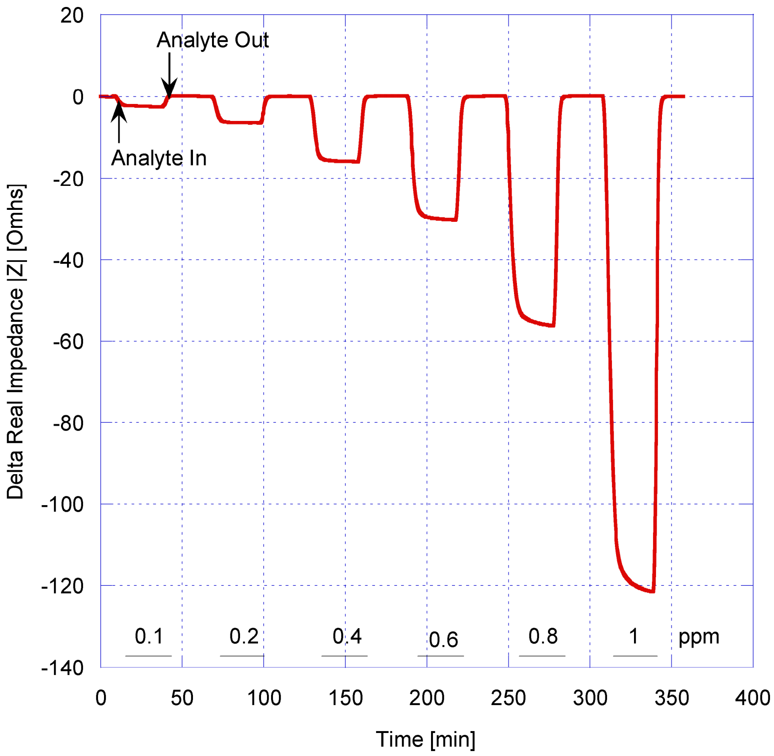

Figure 4.5 Change in Resistance of RFID Sensor to Increasing Concentration of Ethylbenzene in an Aqueous Baseline Solution of pH = 1

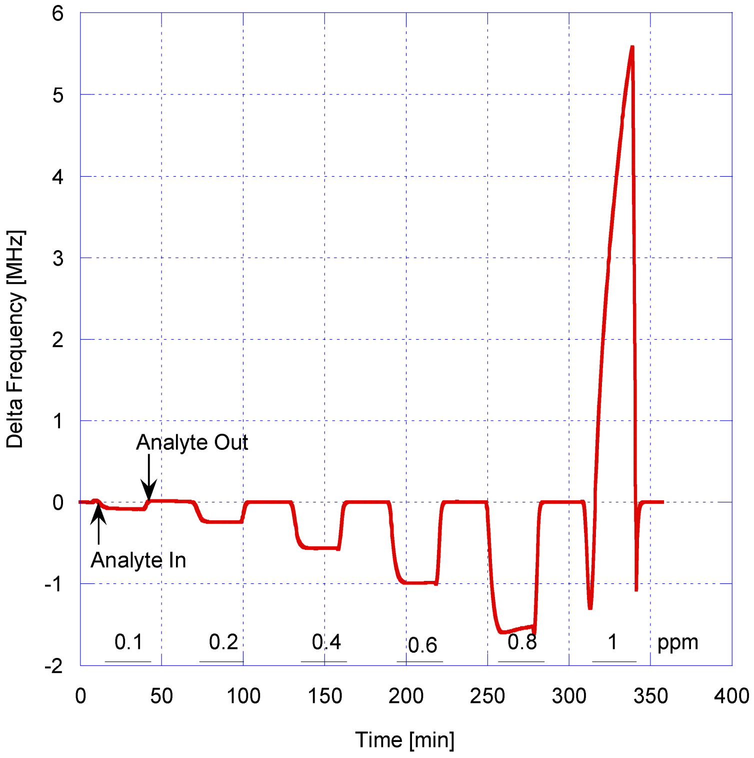

Figure 4.6 Change in Frequency of RFID Sensor to Increasing Concentration of Ethylbenzene in an Aqueous Baseline Solution of pH = 1

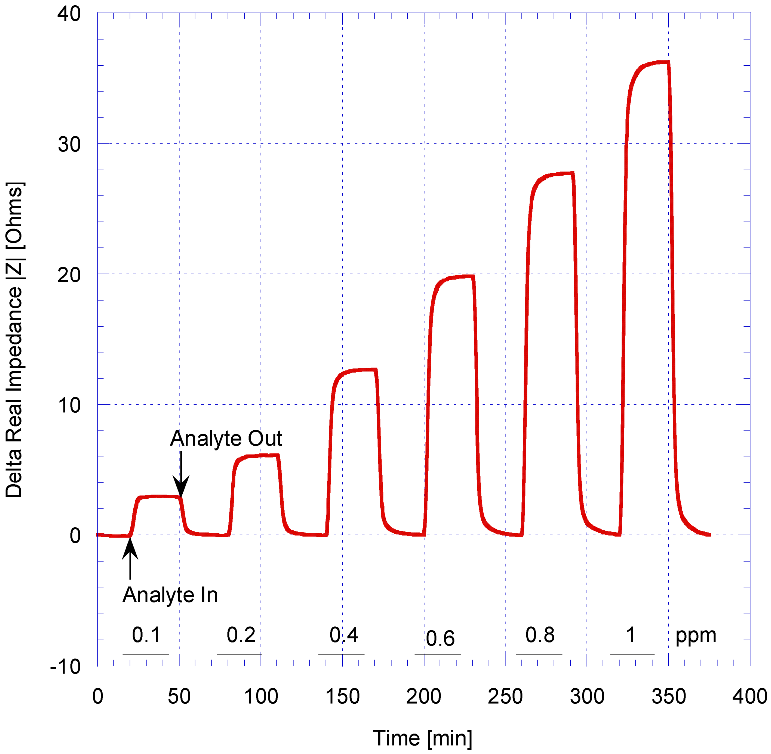

Figure 4.7 Change in Resistance of RFID Sensor to Increasing Concentration of Ethylbenzene in an Aqueous Baseline Solution of pH = 3.5

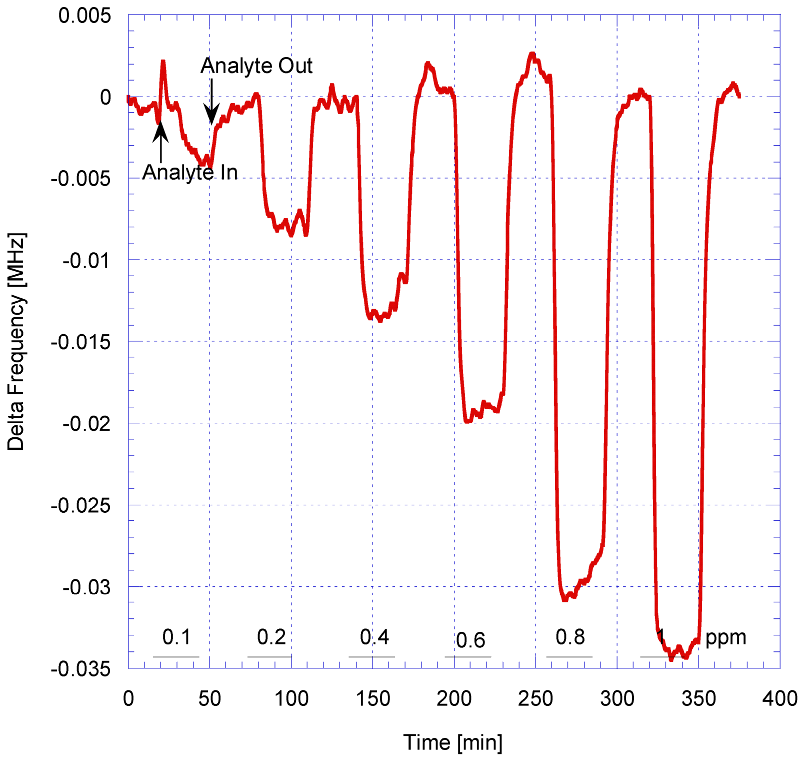

Figure 4.8 Change in Frequency of RFID Sensor to Increasing Concentration of Ethylbenzene in an Aqueous Baseline Solution of pH = 3.5

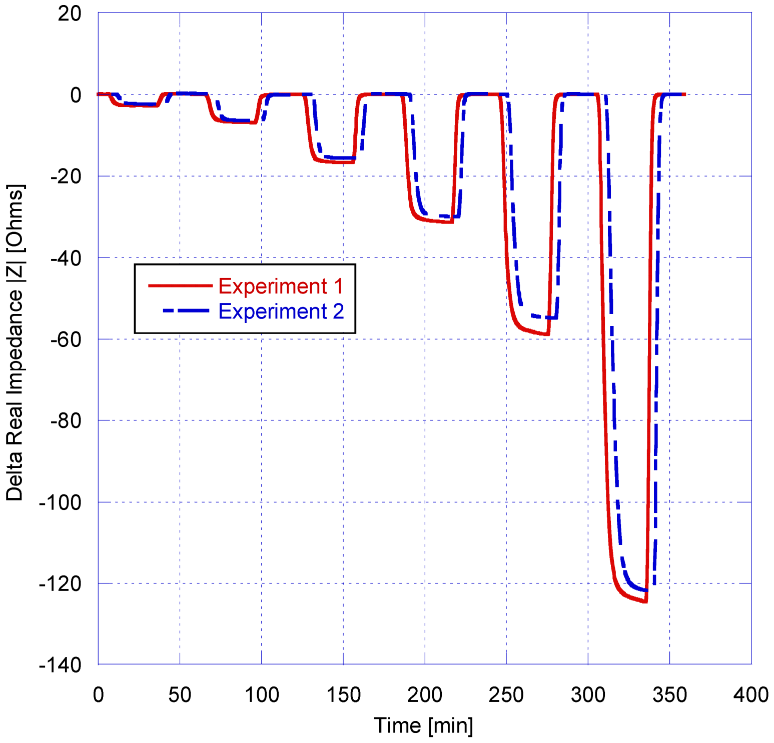

Figure 4.9 Comparison of Two Experiments of Increasing Concentrations of Toluene in an Aqueous Baseline Solution of pH = 1. Injection and flush times have been shifted for comparison purposes.

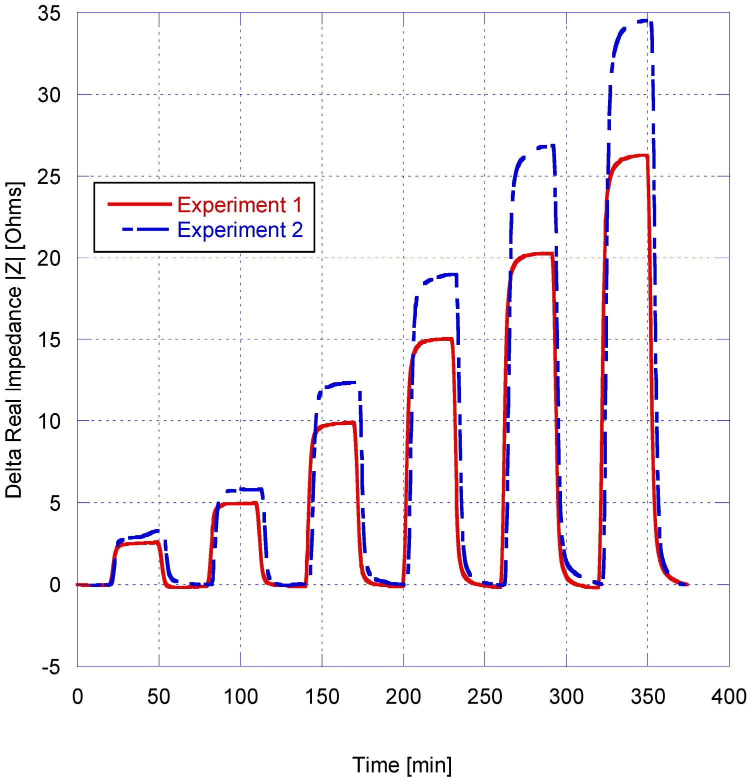

Figure 4.10 Comparison of Two Experiments of Increasing Concentrations of Toluene in an Aqueous Baseline Solution of pH = 3.5. Injection and flush times have been shifted for comparison purposes.

4.3 Comparison and Effect of the Solution pH

A difference in the response of the RFID tag sensor for different pHs of the baseline solution has been observed. Analysis from MacDiamard, et al. [31] provides more details as to the reason for the different responses. The protonation that occurs in the reaction of the acidic solution with PANi greatly increases the conductivity. When the solution has a pH greater than 4 (closer to neutral), the conductivity remains very low, in the order of $10^{-10}\left(\frac{1}{\Omega * cm}\right)$. As the pH of the solution becomes more acidic, a region between pH values of 4 and 2 exhibits a linear increase in conductivity. Once the solution becomes more acidic with a pH of 2 or less, the conductivity again stabilizes with a value near $10^{0}\left(\frac{1}{\Omega * cm}\right)$.

The value of conductivity of the polymer greatly affects the geometry of the RFID tag, which in turn affects the response observed in the experiments. Table 4.1 details what typically happens as the conductivity increases, decreasing the number of the turns and increasing the width of the traces and the length of the coil. These values are calculated using the equations described in Ch. 2 for **R** and **L**, the resistance and inductance associated with the RFID tag.

	Bare Tag	**Low conductive polymer**	**High conductive polymer**
R	334.6153846	178.4615385	89.23076923
L	2.13269E-06	1.12468E-06	1.24986E-08

Parameters changed by increase in Conductivity of Polymer			
length	0.075	0.08	0.2
number of turns	8	6	1
width	0.0002	0.0004	0.002

Table 4.1 Change in resistance and inductance of RFID tag as conductivity increases

Current experiments were performed in the linear region (pH = 3.5) and in the saturated region (pH = 1). Figures 4.11 and 4.12 show the change in resistance versus concentration of toluene. Figures 4.13 and 4.14 show the change in frequency versus concentration of toluene. Similar results were seen for ethylbenzene. A baseline solution of pH = 3.5 results in an increase in resistance when interacting with the increasing analyte concentration. This can be explained as a result of the solution pH increasing further away from the linear region for the conductivity of PANi, and into the lower stable region. In this lower region, the low conductivity of PANi results in an increase of resistance as analyte sorbed into the polymer layer. As concentration increases, the response of the sensor increases. The increase in resistance can be attributed to both the changing pH of the analyte solution for each concentration of the analyte, as well as to the analyte sorbing into the polymer.

In comparison, a baseline solution of pH = 1 results in a decrease in resistance when interacting with increasing analyte concentration. This can be explained by the baseline solution placing the conductivity of PANi in the saturated linear region. Increasing analyte concentrations do not increase the pH of the solution to a value that causes a shift to the linear region of the conductivity of PANi. Since the conductivity remains relatively constant and much higher than the experiments at a pH = 3.5, the decrease in resistance is attributed to the PANi acting like a short across the traces of the tag. Therefore, the increasing analyte concentration adsorbs into a steady layer of PANi with a pH = 1, resulting in larger decreases due to the shorted traces acting like a large sheet resistor.

It should be noted that while changes in frequency are noted for both pH values, the increased conductivity has a negative impact on the response of the RFID tag / planar inductor. Using the baseline solution of pH = 1 shifts the resonant frequency from near 20 MHz towards 80 MHz with a large change in the inductance value. While this increase in resonant frequency does not have a major impact on the current measurements, it is undesirable for insertion into a full RFID system because it will shift the resonant frequency of the tag outside of the allowable bandwidth of the reader, rendering the tag useless. Use of the 3.5 pH baseline solution keeps the resonant frequency near the original resonant frequency, which is desired for future implementation as a wireless sensor.

Independent measurements of the pH of each solution were taken with a pH meter. Adding analyte to the acidic baseline solution caused an increase in overall pH of the solution since the analytes are more basic than the baseline solution. Therefore, the higher the concentration of analyte, the higher the pH of the solution became. To increase detection sensitivity for a wide range of concentrations, it is recommended to perform all experiments near a pH of 1.

While the results are noted to be repeatable, a true error analysis of the experimental data is not provided. The magnitude of error for the change in resistance is noted to increase with an increase in concentration. However, there was no independent measurement of the concentration of each solution to produce the error data.

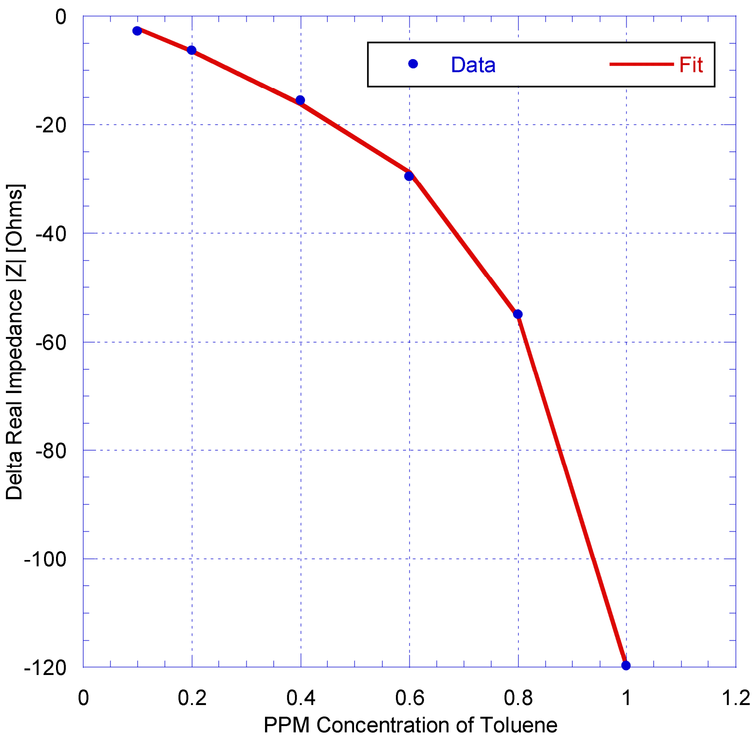

Figure 4.11 Change in Resistance versus Increasing concentrations of Toluene in an Aqueous Baseline Solution of pH = 1

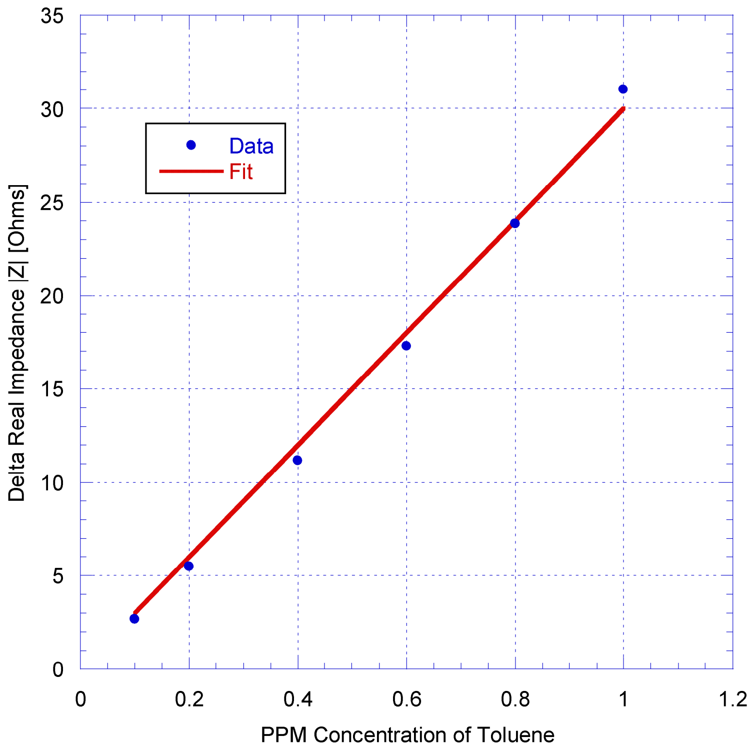

Figure 4.12 Change in Resistance versus Increasing concentrations of Toluene in an Aqueous Baseline Solution of pH = 3.5

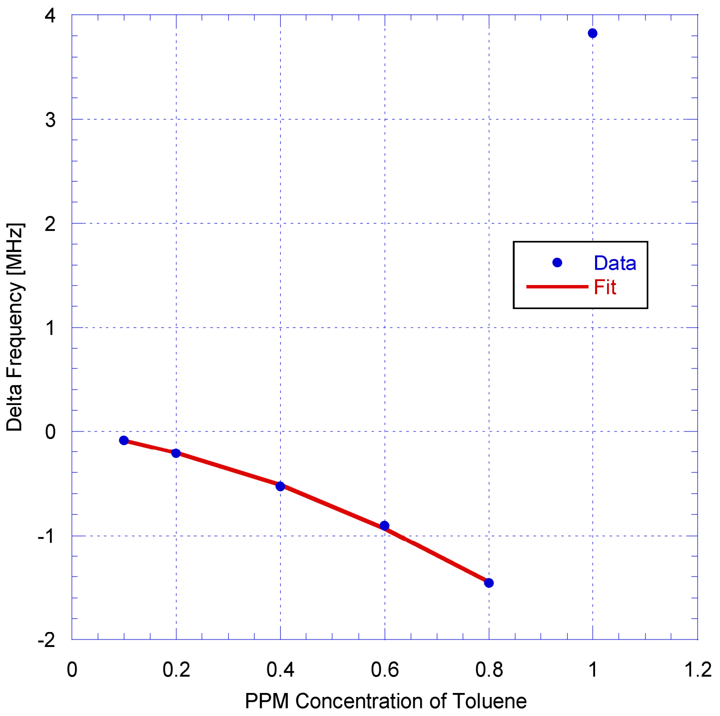

Figure 4.13 Change in Frequency versus Increasing concentrations of Toluene in an Aqueous Baseline Solution of pH = 1

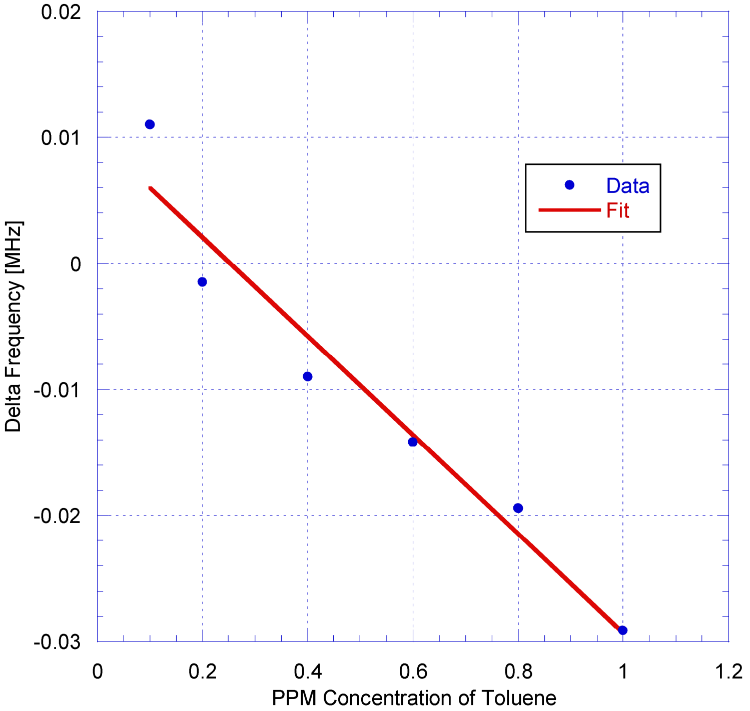

Figure 4.14 Change in Frequency versus Increasing concentrations of Toluene in an Aqueous Baseline Solution of pH = 3.5

4.4 Partial Selectivity

Experiments were run with both toluene and ethylbenzene. Both analytes provided similar responses in terms of magnitude and response time. To be able to properly differentiate between the two analytes, a comparison between the change in resistance and the change in frequency are both needed. Toluene and ethylbenzene are both polar compounds with similar chemical structures, so their interaction with the polymer layers is very similar. When in a baseline solution of pH = 1, it is difficult to differentiate between the two analytes due to each of the solutions having similar conductivities. However, when comparing the results for a baseline solution of pH = 3.5, the results become slightly more distinguishable. Ethylbenzene provides a higher increase in resistance, with a larger decrease in frequency as well. This is because ethylbenzene provides a larger shift in pH than toluene to the overall solution. The larger shift in pH coupled with the interaction of the ethylbenzene with the polymer layer creates the larger shifts. These results prove that partial selectivity can be achieved for this sensor. To increase the selectivity of this sensor, it is recommended to perform all experiments in the linear region of the conductivity, i.e. near a pH of 3.5.

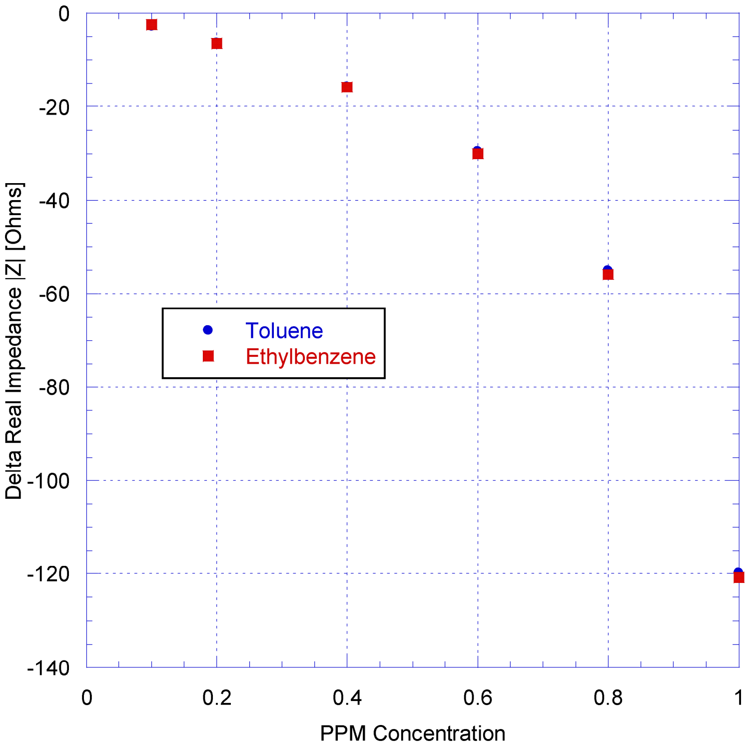

Figure 4.15 Change in resistance versus increasing concentration of both toluene and ethylbenzene for an aqueous baseline solution of pH = 1

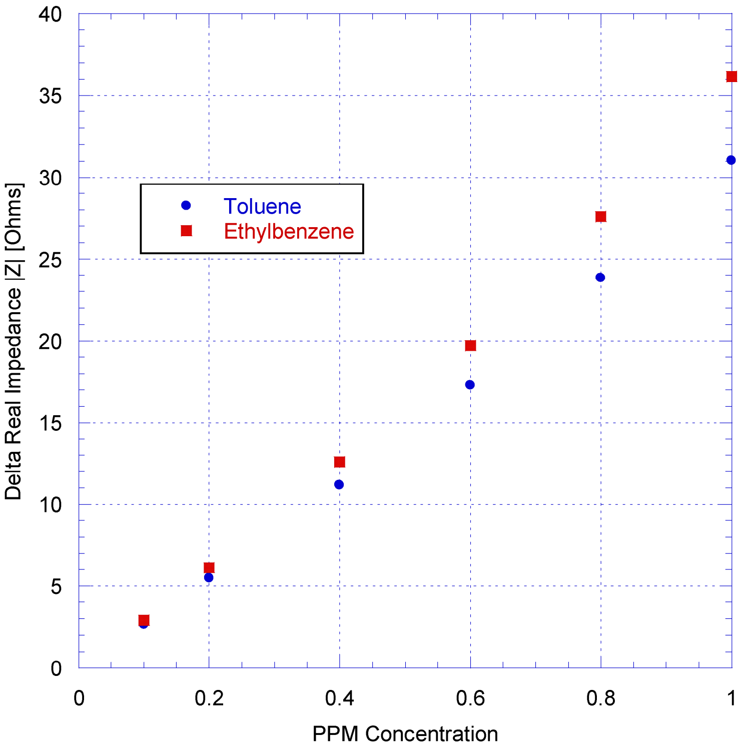

Figure 4.16 Change in resistance versus increasing concentration of both toluene and ethylbenzene for an aqueous baseline solution of pH = 3.5

4.5 Limit of Detection and Response Time

Two other important characteristics of this sensor are the limit of detection and the response time. Limit of detection, the lowest amount of chemical able to be detected, is defined by [10]:

$$LOD = \frac{3\delta}{S} \qquad (4.1)$$

where δ is the noise of the measured signal and S is the sensitivity of sensor. The sensitivity of each sensor configuration is determined by the slope of the response when fitting the measured shift in resistance versus the concentration of analyte. The noise of the measured signal is defined as the level above or below the steady state response. Limit of detection varies for analyte / baseline solution pairs. Table 4.1 gives the average noise and sensitivity measured for each experimental setup, along with the limits of detection that correspond. The noise of each configuration is found by averaging the noise on the steady state response of the measured resistance for each concentration. The noise for each concentration is then averaged to provide an overall average noise for the sensor with a given baseline solution and analyte. The sensitivity of each configuration is found from the fit to the measured data. The limit of detection for toluene is 1.4 ppb in a baseline solution of pH = 1, and 6.24 ppb in a baseline solution of pH = 3.5. The limit of detection for ethylbenzene is 0.9 ppb in a baseline solution of pH = 1, and 8.3 ppb in a baseline solution of pH = 3.5. Regardless of the baseline solution, the low limits of detection indicate that detecting trace amounts of either chemical is possible. The low limits of detection also prove that this sensor would be able to detect the levels of maximum daily allowance of toluene and ethylbenzene as defined for drinking water by the EPA [42] and for waste water by the state of Wisconsin [43]. Experiments with lower levels of each analyte were not attempted due to the inability to independently measure and verify concentrations lower than 100 ppb.

		δ	**S**	**LOD [ppb]**
pH = 1	Toluene	0.087906	190.283	1.38593
	Ethylbenzene	0.056521	190.283	0.891113
pH = 3.5	Toluene	0.062364	30.003	6.235778
	Ethylbenzene	0.095884	34.671	8.296614

Table 4.2 Measured values of noise and sensitivity for each sensor configuration to provide Limit of Detection (LOD).

Response time is defined as the time it takes the sensor to respond to 90% of its steady state value. In determining the response time of the sensor, 90% of steady state is calculated for each experiment and analyte concentration. When the time taken to reach this 90% value is found, the data is averaged to find the average response time of the sensor to each concentration level. As analyte concentration increases, it takes the sensor longer to reach 90% of its steady state value. This is due to fewer sites in the polymer for the analyte to sorb into. The response time for the sensor sensing toluene in a baseline solution of pH = 1 is 7.76 min, and 5.2 min for a baseline solution of pH = 3.5; with ethylbenzene as the analyte, the response times are 6.9 min and 5.32 min for baseline solutions of pH = 1 and pH = 3.5 respectively. The fast response times seen in the experiments are ideal for use as a chemical sensor.

The results shown here provide evidence that an RFID tag / planar inductor liquid-phase chemical sensor is possible. Results from the present measurements varied for different pH values due to the changing conductivity of PANi.

5 SUMMARY, CONCLUSION, AND FUTURE WORK

5.1 Summary

The objective of this work was to investigate the use of an RFID tag / planar inductor as a chemical sensor in liquid-phase environments. Focusing on the planar inductor coil of an RFID tag as the sensor platform, a dual layer film was investigated for high sensitivity of organic compounds. To improve sensitivity, a conductive polymer was introduced that allowed for different results dependent on the pH of the aqueous baseline solution. Fast sensor response was observed for both analytes, as well as good reversibility. From the responses shown, suggestions were made to improve either the sensitivity or the selectivity of the sensor.

An overview of chemical sensors was first presented, with an emphasis on RFID tag / planar inductor chemical sensors. Equivalent circuit analysis on both bare and coated RFID tags was presented to better understand how analyte sorption into the polymer layer affects the lumped elements of the RFID / planar inductor equivalent circuit. The resonant frequency for a coated tag and the related change in frequency were derived to predict which elements would provide the highest amount of sensitivity. In this analysis, higher order terms were neglected as the chemical sorption was assumed to be the only effect on the response of the sensor.

Experiments were performed to determine the use of an RFID tag / planar inductor sensor in liquid-phase environments. A liquid flow cell was designed and fabricated to properly test the sensor. A dual layer film consisiting of poly(epichlorhydrin) (PECH) under polyaniline (PANi) was implemented as the sensing layer. These polymers were chosen for their known sensitivity to the analytes toluene and ethylbenzene; PANi was specifically chosen for its conductive nature. The specific analytes were chosen due to the harmful nature that these chemicals have on humans, along with the maximum daily allowances of these in both drinking and waste water. The RFID tags were characterized using a vector network analyzer to determine the properties of the bare tags. The tags were then spin-coated with the dual layer film. Data was collected from the coated tags for varying concentrations of analyte (toluene or ethylbenzene) in baseline solutions of two different pHs.

Results were presented proving the use of an RFID tag / planar inductor as a liquid-phase chemical sensor platform. Typical sensor responses showing shifts in both resistance and resonant frequency from exposure to toluene and ethylbenzene were presented. Analysis on the responses for the differing pH of the baseline solution was also presented showing how the protonation of PANi affects the sensing ability. The sensor with the dual-layer coating showed partial selectivity dependant on the conductivity of PANi. The limit of detection and response time were both defined and presented for toluene and ethylbenzene for the current measurements.

5.2 Conclusion

An ideal chemical sensor should exhibit reversibility, high sensitivity, high selectivity to a given analyte, and a fast response time. In creating a chemical sensor, there is often a compromise between these parameters. In this work, it has been shown that a dual-layer polymer coating of PECH and PANi provides the necessary sensing layer for the detection of organic compounds in aqueous environments.

Typical sensor responses show very high sensitivity to both toluene and ethylbenzene. Shifts in both resistance and frequency can be used together to properly identify and quantify the analyte being detected. The addition of PANi provided added sensitivity as the traces of the planar inductor began to effectively short out with increasing conductivity of the polymer. Similar response times were also noted for both analytes, with the response time increasing as analyte concentration increased. The similar sensor responses to both analytes are likely due to the similar chemical structure of the analytes. Partial selectivity is necessary for a chemical sensor to determine which chemical is sorbing into the polymer. The partial selectivity noted between the two analytes for the aqueous baseline solution of pH = 3.5 is due to the changing conductivity of PANi. While the dual-layer polymer system provides good sensor response, different films should be investigated that have high sensitivity and a fast response time, but increase the selectivity between the target analytes.

Changing the pH of the baseline solution provided different sensor responses. This is due to the different level of protonation of PANi that occurred between the baseline solution and the polymer layer. As the pH of the baseline solution decreases, becoming more acidic, more hydrogen atoms are available to bond with the amide nitrogens in the PANi. When the bonding occurs, this allows for increased charge mobility through the film, further increasing the conductivity of the film. Lower pH solutions increased the conductivity of PANi to a level that drastically changed the behavior of the tag, shifting the resonant frequency from around 20 MHz to 80 MHz. This occurs since the PANi acts like a conductive sheet over the traces, effectively shorting out the traces. The large shift in frequency is related to a decrease in both the inductance and the capacitance of the tag. While using the baseline solution with a pH = 1 produced a very sensitive response, this is not ideal for implementation as a chemical sensor in RFID systems due to the large shift in the resonant frequency. This shift would cause the tag to no longer work with the previously designed reader. While the results with the aqueous baseline solution of pH = 1 provided the largest sensitivity, the results from the aqueous baseline solution of pH = 3.5 also provided highly sensitive results. As the resonant frequency did not shift in the baseline solution of pH = 3.5 and because the sensor exhibited a high sensitivity, the selected pH range represents the ideal operating range for implementing a full RFID sensor system.

If the baseline solution’s pH is decreased to increase the conductivity of PANi while keeping the conductivity in the linear range [31], higher sensitivity will be seen due to the increased conductivity and the continual increase in pH from increased analyte concentration. However, the limit of detection is increased for higher pH values, making it difficult to detect low quantities of analyte. Limit of detection for an aqueous baseline solution of pH = 3.5 was 6.24 ppb for toluene and 8.3 ppb for ethylbenzene, which are both still well below the hazardous limits allowed by the EPA [42] and the Wisconsin DNR [43]. To create an ideal chemical sensor with high sensitivity, good selectivity, and low limit of detection, similar preparation of the dual layer coated RFID tags should be implemented with a baseline solution of pH = 3.5.

5.3 Future Work

While the results prove the use of a liquid phase RFID tag / planar inductor chemical sensor is possible, there are many opportunities to further this work. The first suggestion for future work is to implement the wireless capability of this sensor by integrating this into an RFID system. This would allow for the capability to sense chemicals in a liquid environment without having to prepare a sample of the solution to be tested. Results could be immediately correlated to chemical concentration, further decreasing the amount of time necessary to determine if hazardous concentrations of chemicals are present. Once the concept is tested at a fixed configuration, further tests that change the orientation of the reader to the tag would be necessary to ensure proper operation without a decrease in coupling or distance between the reader and the tag.

The measured results were due to changes in the geometry of the planar inductor for the given RFID tag when the polymer became more conductive. The specific tag used in the experiments was chosen for its size as a sensor and for rapid availability. However, RFID tags of different dimensions or geometries may produce improved results for use as a chemical sensor. Different geometries would need to be tested to determine if a different geometry, such as a square planar inductor or another RFID tag design, would produce higher sensitivities, increased read range, or modify another desired parameter.

A polymer that would allow for similar conductivity but not require any sample preparation, i.e. no acid in the baseline solution, would be ideal. The investigation and development of such a polymer would be necessary, followed by testing to confirm that it provides similar results to those seen in the present work. The polymer would need to adhere to the sensor surface and remain on the sensor when subjected to an aqueous baseline solution. The removal of the additional polymer layer will allow for the conductive nature of the new polymer to have an increased effect on the planar inductor's geometry.

Finally, to implement the RFID tag / planar inductor sensor as an ideal chemical sensor platform, it is necessary to increase the selectivity between differing analyte species. Current experiments show partial selectivity between toluene and ethylbenzene depending on the pH of the baseline solution. It is desired that the selectivity between these analytes be noticeable regardless of the pH of the solution. This could be done through the removal of the sample preparation, but further investigation would be necessary to ensure that the sensor is capable of differentiating between different analyte species.

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APPENDIX A: Spin Coater Settings

Below are the spin coater settings used during the present experiments to uniformly coat the RFID tags. These specific settings were chosen from past experience in the Microsensor Research Lab, as well as from testing to determine which recipes gave uniform polymer coatings. Setting 1 was used for coating the base layer of PECH, while Setting 3 was used to coat the conductive polymer PANi onto the device.

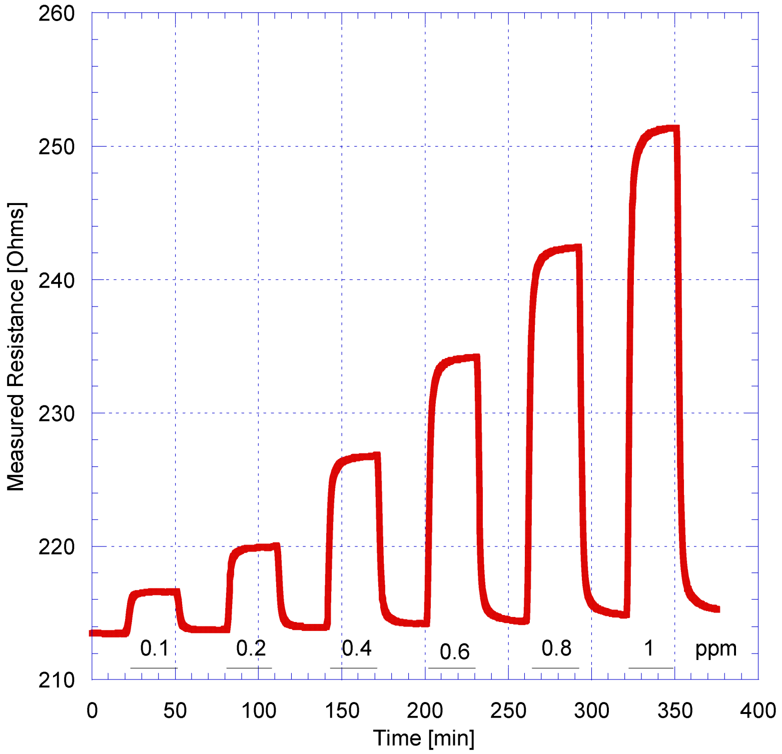
Setting 1:
RPM 1: 0100
RAMP 1: 0003
TIME 1: 0002
RPM 2: 0100
RAMP 2: 0003
TIME 2: 0002
RPM 3: 5000
RAMP 3: 0003
TIME 3: 0050
RAMP 4: 0003

Setting 3:
RPM 1: 0100
RAMP 1: 0003
TIME 1: 0002
RPM 2: 0100
RAMP 2: 0003
TIME 2: 0002
RPM 3: 5000
RAMP 3: 0003
TIME 3: 0040
RAMP 4: 0003

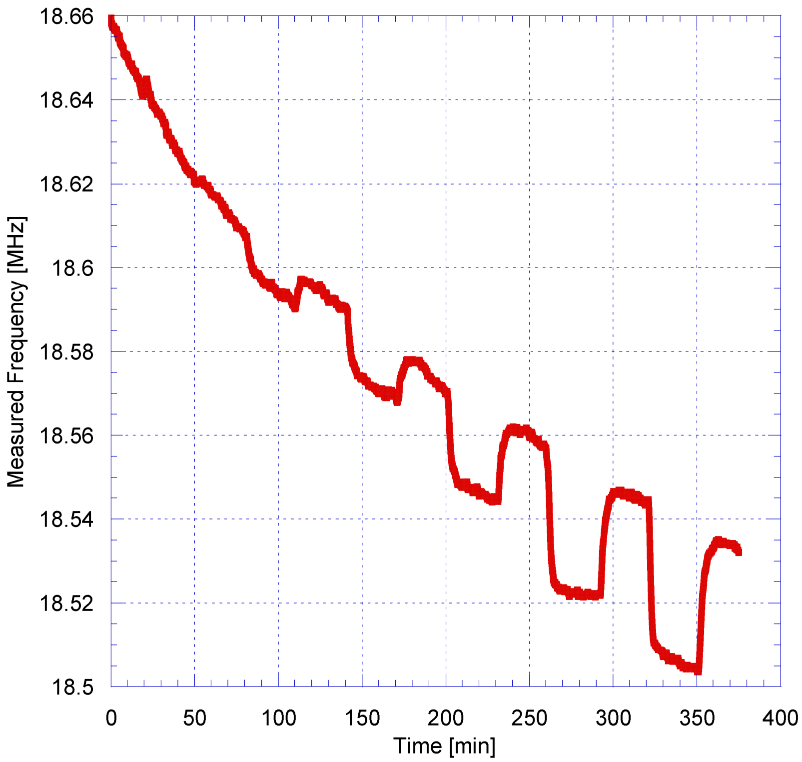
The parameters for each recipe include RPM, how fast the chuck spins during the segment, TIME, how long the chuck remains at the given speed, and RAMP, the approximate amount of time it takes to reach the desired speed. RAMP 4 is defined as the approximate time it takes for the chuck to come to a complete stop at the end of the coating cycle.

APPENDIX B: Raw Data and Baseline Correction

Below are examples of raw data achieved during the experiments. While sometimes the raw data was clean, there was often some baseline drift that needed to be properly corrected. Also, baseline correction provided a tool to show the magnitude of changes when the chemical sorbed into the polymer. Baseline correction is performed by a linear interpolation between when one concentration of analyte is introduced until the next concentration is introduced.



Raw data of RFID tag: resistance during exposure to toluene using a baseline solution of pH = 3.5



Raw data of RFID tag: frequency during exposure to toluene using a baseline solution of pH = 3.5

The baseline corrected data is measured as the change in each parameter, such as change in resistance or change in frequency, from the baseline of the measurements. The resulting baseline corrected data can be correlated to Figure 4.7 for resistance and Figure 4.8 for frequency.