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Fluid Manipulations Using a Piezo Electric Transformer for Sensing and Spray Generation Applications

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FLUID MANIPULATIONS USING A PIEZOELECTRIC TRANSFORMER FOR SENSING AND SPRAY GENERATION APPLICATIONS

by

Zeinab Ramshani

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in partial fulfillment of the requirements
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FLUID MANIPULATIONS USING A PIEZO ELECTRIC TRANSFORMER FOR SENSING AND SPRAY GENERATION APPLICATIONS

Zeinab Ramshani, Ph.D.
Western Michigan University, 2017

A steady effort has been made on the development of fluid manipulation techniques for sensing and actuating systems. Conventional techniques of fluid manipulation for sensing and spray generation purposes, often need trained staff or high input power and they are complicated, time consuming and expensive. Therefore, it is necessary to develop new systems which can overcome these drawbacks.

In this dissertation, the author has developed piezoelectric-based systems for fluid manipulation. The focus of this dissertation involves novel approaches of enhancing the sensing and actuating systems using the piezoelectric devices. This includes designing a system, which theoretically can overcome the limitations associated with conventional fluid manipulation systems, fabricating the device and examining the functionality of the system to prove the claim.

The purpose of the first project of this research work was to design and fabricate a piezoelectric based system to enhance the sensitivity of the system towards the sensing of toxic materials in liquid media. The functionality of the designed sensing system was investigated towards several toxic heavy metals including lead, cadmium, nickel and mercury. The SH-SAW sensor was fabricated on a 64° YX-LiNbO₃ piezoelectric substrate using photolithography techniques and placed in the sensor groove of an acrylic based material flow cell. Then, varying concentrations of target analytes were injected into the flow cell using a programmable syringe pump. A network analyzer was used to measure the phase response ($S_{21}$).
of the SH-SAW sensor towards the test analytes. System control, data acquisition and post processing of the network analyzer measurements was performed using a LabView™ based application. The significance of this research was based on the contribution that this sensing system could enhance the detection of the toxic heavy metal ions to pico molar concentration levels while conventional methods often work in the micro molar concentration levels.

Further, a piezoelectric based system which can be utilized for spray generation from a desired liquid was designed and fabricated. A linear 128° Y-cut lithium niobate (LiNbO₃) crystal was used and a 3D printed stand was designed to pin the piezoelectric transformer on the second resonance standing wave nodes. The piezoelectric transformer (PT) was actuated by a signal generator connected to a radio frequency (RF) amplifier. To generate the spray, various aqueous solutions prepared using deionized (DI) water was filled in an adjacent reservoir and a paper bridge was placed from the reservoir and in contact with the surface of the PT. The generated piezoelectric driven spray resulted in a broad area, uniform, continues spray appropriate for coating applications. The spray generation system also made it possible to generate the spray out of the liquid by applying around 15 V_{amp}, AC input voltage amplitude, while traditional techniques typically require around 100 V_{amp} for spray formation.

Finally, the PT driven spray generation technique was used for membrane coating applications. Different polymers such as poly(allylamine hydrochloride) (PAH)/ poly(styrene sulfonate) (PSS) and poly(diallyl-dimethylammonium chloride) (PDADMAC) were sequentially sprayed on to a polycarbonate track-etched (PCTE) membrane. The polymer coated membrane was tested towards water permeability and ion rejection ratio to investigate the functionality of this novel spray generation system for membrane coating purposes.
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Finally, I would like to dedicate this dissertation to my family. To my dad who may not always agree with me but when the time comes, supports me the most. To my mom and her unconditional love. To my brothers who have taken care of all my responsibilities at home, while I was pursuing my dreams overseas.

Zeinab Ramshani
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CHAPTER I

INTRODUCTION

1.1 Motivation

A steady effort has been made on the development of fluid manipulation techniques for sensing and actuating systems. Conventional fluid manipulation mechanisms by external pressure using pumps and air pressure are simple, but not precise\(^1\). Ultrasonic standing waves produced by piezoceramic and sound reflector, have been used for fluid manipulations in a variety of applications as a more accurate solution\(^2\). Nilsson \textit{et al.} \(^3\) have used this method in separation of plasma and erythrocytes in blood stream based on particle gathering in the nodes of the propagating ultrasonic standing wave. In this dissertation, the author focuses on two aspects of the fluid manipulation applications: sensing and spray generation systems.

Among research developments in sensing systems, heavy metal detection systems have been receiving an increasing attention due to its adverse effects in aquatic and atmospheric ecosystems, even at the micro- or nano-molar concentration levels\(^4,5\). In the case of aqueous systems, this eco- and phyto toxicity on vital microorganisms is influenced by environmental factors\(^6\). Traditional detection methods for toxic heavy metals, mostly found in their ionic form in nature, include spectrometric sensing systems or biological / chemical sensors\(^7,8,9,10,11,12,13\). Spectrometric sensing systems work based on the interaction between applied electromagnetic radiation and the heavy metal ions, while the chemical and biological sensors rely on the change on a specific ligand’s functionality in the presence of the heavy metal ions. However, these techniques often need trained staff and they are complicated as well as time consuming\(^14\). Therefore, it is necessary to develop sensing systems that are easy-to-use, cost effective, highly sensitive and employ rapid detection techniques.
Various mechanisms can be used to manipulate and atomize fluids, from simple approaches like a pneumatic atomizer, in which there is no control on the droplet size, to more precise ones such as an acoustic based atomizer. Surface acoustic wave devices are proven to work well for atomizing the desired aqueous sample in chemical analysis approaches and mass spectrometry. However, they are often complicated to fabricate and need around 100 V\textsubscript{amp} input voltage\textsuperscript{15}. To get an electrically driven spray, approximately 1-5 KV\textsubscript{amp} has to be applied to the liquid to form the droplet plume in electrospray systems\textsuperscript{16}. Among all the drawbacks in conventional spray generation systems, the high amount of required applied voltage can be a significant reason for illustrating the need for more research in fluid manipulation.

Piezoelectric devices produce mechanical strain under applied electrical field which results in propagating mechanical vibrations\textsuperscript{17}. Acoustic waves have been used to manipulate the liquid medium in sensing technologies, due to its benefits such as small sample volume, high sensitivity and bio compatibility\textsuperscript{18,19,20}. The high sensitivity arises from the large electromechanical coupling factor of the piezoelectric crystal\textsuperscript{21}. Moreover, the aforementioned features make piezoelectric devices an apt choice in actuating systems such as aerosolization. The mechanical vibration along with the large polarization produced on the surface of the piezoelectric crystal can be used to overcome the liquid film surface tension and break it into the droplets.

\textbf{1.2 Author’s Contributions}

In the first project, described in chapter3, the author designed and fabricated a surface acoustic wave device, contributed in synthesis of proper sensing layer and conducted some experiments in order to investigate the functionality of the system towards lead, mercury, cadmium and nickel ions in pico molar concentration in water. From this part of research, author published a decent journal paper along with 5 conference papers.
In the second project, described in chapter 4, author designed a novel piezoelectric transformer based spray generation system. Author was responsible for design and fabrication of the proper piezoelectric transformer and stand fabrication for fluid manipulation and spray generation from a liquid reservoir. The author then performed some experiment to measure the various spray parameters such as current and voltage and to study the effect of liquid properties on the generated spray characteristics. From this research work, author published an intellectual property, a patent and a decent journal paper.

In the third project, described in chapter 5, author found a practical use for the PT driven spray system. The capability of the system was examined towards the membrane coating. The author conducted different experiments to collect adequate data which was proving the reliability of this approach. From this part of the research, author was published an intellectual property, a patent and a paper.

Overall, the author’s research work has resulted in two intellectual properties disclosures, two patent applications, three high quality peer reviewed journal and six conference publications mentioned in Appendix A. The results of the projects have been published in prestigious journals such as Sensors and Actuators: B Chemical; Applied Physics Letter and Analytical Methods. The research outcomes have been shared with other scholars in this field during the author’s presentation and proceedings in international conferences such as IEEE Sensors Conference (2013, 2015, 2016), Electro/Information Technology (EIT) (2013), International Meeting for Chemical Sensors (IMCS) (2014), Frequency Control Symposium & the European Frequency and Time Forum (FCS) (2015) and Electrostatic Society of America (ESA) (2016). The author also was awarded the All-University Graduate Research and Creative Scholar Award for 2016-17 by Western Michigan University.
1.3 Dissertation Organization

This dissertation presents details of the research projects that was performed, including developing piezoelectric based systems for fluid manipulation and investigating the capability of the designed piezoelectric based systems for sensing applications and spray generation.

In Chapter 2, the literature review is provided. This chapter presents a brief introduction to conventional fluid manipulation systems used for sensing and spray generation. The basic definition of sensor followed by previous sensing systems that have been successfully used for toxic heavy metal detection in liquid media are discussed. Traditional techniques of spray generation are also reviewed in this chapter. The drawbacks of these systems which led the author to develop a piezoelectric based fluid manipulation system in this dissertation, are also included in the discussions.

In Chapter 3, a project on developing a piezoelectric sensing system is presented. An efficient piezoelectric transformer was fabricated for the detection of heavy metal compounds. An acrylic flow cell, which consists of inlet and outlet ports for the microfluidic chamber as well as polydimethylsiloxane (PDMS) based microfluidic channels was used to provide a user friendly, re-usable sensing system. A chemical sensing layer was utilized to selectively bind to heavy metal ions. The capability of the system for detecting varying concentrations of heavy metal ions, such as lead (Pb), cadmium (Cd), mercury (Hg) and nickel (Ni) in liquid environments, through phase shifts in the frequency response of the piezoelectric sensor, was studied. This work demonstrated the capability of the developed system to detect heavy metal compounds at pico molar concentration levels.

In Chapter 4, a project for developing a novel spray generation system using a piezoelectric transformer is presented. The author demonstrated the use of a piezoelectric transducer to induce the generation of a broad area electrospray. A piezoelectric transducer was designed and top and bottom electrodes was patterned to generate adequate output voltage from
an applied input voltage. A proper PT stand was designed and 3D printed to access the piezocrystal second resonant frequency. A continues broad area spray was formed by providing a persistent liquid film using a paper bridge connected to a liquid sample reservoir. The effect of various liquid parameters on the generated spray was studied.

In Chapter 5, the piezoelectric transformer based spray production system was used for membrane coating. The capability of the system for spray formation out of some high demand coating materials was investigated. Polymer coating of a track etched membrane was chosen due to the recent high demand. Solutions of these polymers were sprayed using the PT driven spray system. Coated membranes were tested for the water permeability and ion rejected ratio. The outcomes will be presented to indicate the abilities and limitations of the system for this purpose.

Finally, in Chapter 6, a conclusion of the research work and suggestions for the future works are presented.
1.4 References


10 Quang, Duong Tuan, and Jong Seung Kim. "Fluoro-and chromogenic chemodosimeters for heavy metal ion detection in solution and biospecimens." *Chemical reviews* 110, no. 10 (2010): 6280-6301.


CHAPTER II

LITERATURE REVIEW

2.1 Introduction

Fluid manipulation at the microfluidic scale plays a significant role in developing lab-on-a-chip functional technologies. These miniaturized structures, need small volumes of reagents and result in a fast and accurate response due to their enhanced sensitivity that is critical for sensing systems\(^1\). In this chapter, the author has reviewed conventional methods used for fluid manipulation in sensing or spray generation systems. After a brief explanation of sensor basics and the elevating need for improvements in toxic heavy metal sensing systems, due to their environmental drawbacks, the author introduces some traditional methods of toxic heavy metal sensing systems (spectrometric, chemical/biological and acoustic sensors). The reasons behind the author’s choice of the sensing method further in this dissertation, is also discussed.

The well proved techniques of spray generations are also reviewed in this chapter. Despite all the methods described (pneumatic, acoustic and electrical spray), the author explains the necessity for further improvement in spray formation technology for specific applications.
2.2 Fluid Manipulation Techniques for Sensing Applications

This section provides a brief historical background about conventional fluid manipulation techniques for sensing applications. Sensors mostly produce a mechanical or electrical signal in response to the change in their physical properties. Sensors have been widely used in various applications since their first discovery in the early 19th century\(^2\). Among the different usage of sensors, the author is focusing on the sensing systems that target toxic heavy metal compounds in aqueous media.

2.2.1 Toxic Heavy Metal Deficiencies

Heavy metals are the elements with atomic weight between 63 and 209 g/mol in the periodic table of elements\(^3\). The toxic effect of heavy metals has been a growing concern in the biomedical and environmental industries, and hence a major focus of research in the development of different sensing systems. Although, heavy metals are typically formulated as non-toxic compounds, it has been shown that they can cause serious health issues even at micro molar concentration levels\(^4\).

The rising demand for heavy metals in applications such as plating, mining, solar cells, pharmaceutical and chemical industries intensifies their role as environmental pollutants\(^5,6\). Toxic heavy metals can be released in the environment and pollute the area for a long time during their mining process\(^7\). Some toxic heavy metals are also used to mine the other materials\(^8\). These toxic ions accumulate in human body since they are not biodegradable like organic contaminants\(^9\). In plants, toxic heavy metals can affect the root growth as well as water entry and exit and cause some deficiencies in their physiological functions\(^10\). The extra aggregation of the toxic heavy metals in vegetables from contaminated water can aafect food safety\(^11\). The detection of these heavy metal compounds is thus of utmost importance.
2.2.2 Sensors

An electronic sensor is defined as a device which responds to a stimulant by producing an electrical signal. The sensor converts a physical property to a readable signal which makes it possible to record the data for future analysis. The output of the sensor can be used to trace any changes in amplitude, phase or frequency of the voltage or the current of the electrical signal. Sensors can be classified as active or passive. An active sensor requires additional energy source other than the physical property which being sensed, however a passive sensor does not need any external source of energy for sensing activities.

For example, there are passive and active sensors designed for satellites. Active sensors, such as radar, use the electromagnetic radiation as the external source and compares the sent and received signals to measure the distances to objects. On the other hand, a satellite’s passive sensors may utilize reflected sunlight or thermal radiation.

2.2.2.1 Spectrometric Sensors

Spectrometric sensing systems are categorized as optical sensors, where the sensor is designed to use a light source to detect the changes in the measurand. These sensing systems use electromagnetic radiation and record changes in the intensity as a function of the frequency or wavelength.

After the initial launch of the atomic absorption spectrometer in the 19th century, an enhanced cold vapor atomic absorption spectroscopy (CVAAS) was developed as a technique for heavy metal ion detection. Hatch and Ott transferred mercury ions to the spectrometer optical measurement by neutralizing the ions with stannous chloride to generate the vapor form of mercury. A pure, dry gas such as air or argon is used to carry the mercury vapor. The light
absorption of mercury is directly proportional with the ion concentration. However, any other ions in the inert gas, which can reduce the fluorescence emission, can affect the results.

A faster spectrometric approach for heavy metal detection, when compared to the atomic adsorption technique, is inductively coupled plasma mass spectroscopy (ICP-MS). Argon atoms are ionized by being placed inside an electromagnetic field generated by an RF oscillation circuit producing a plasma discharge. This can ionize an aerosolized heavy metal sample, which is introduced to the discharge and connected to the mass spectrometer for heavy metal ion detection. Micro molar level concentration of heavy metal has also been detected using inductively coupled plasma atomic emission spectrometry (ICP-AES). Excited atoms and ions produced by inductive coupled plasma emit electromagnetic radiation at wavelengths that are related to the specific material.

Even though these methods have reliable results, they are relatively expensive, time consuming and need trained personnel.

2.2.2.2 Chemical and Biological Sensors

A chemo/bio sensor records a readable signal in response to a controlled binding event by combining a chemical/biological sensing element with a transducer. Prasad et al. demonstrated that specific antigen antibody binding can be used to detect low concentrations of environmental and physiological hazardous agents for neural studies. Metal ions can change the enzyme function, suppressing them. The immobility of enzyme oxides or proteins have been used to detect micro molar concentration levels of the toxic heavy metal compounds in liquid media. The need to develop alternative techniques of enzyme based sensors seems to be necessary due to enzyme price, time consuming reactions and the required complex enzyme reactions since the pollutants could not be recognized with a simple enzyme reaction. For this reason, Yamasaki et al. implemented a microbial based sensing system,
for copper detection in water. The presence of copper was found to suppress the bacterial growth and a detection limit was reported to be in the milimolar concentration level. However, it is worth mentioning that the use of microbes in this detector can be hazardous to the user.

2.2.2.3 Acoustic Sensors

In acoustic sensors, the change in the environment can be detected by the investigation of an acoustic wave, which propagates throughout the media. These types of sensors are typically based on piezoelectricity, which involves electrical to mechanical vibration conversion and vice versa. Piezoelectric sensors have been used in various sensing applications for measuring the changes in the propagating acoustic wave characteristics, such as magnitude or phase shift in the frequency response. An example of an acoustic sensor is a quartz crystal microbalance (QCM) sensor, consisting of a quartz crystal and metal electrodes, that shows a shift in resonant frequency with any change in the applied mass. QCMs have been successfully tested for heavy metal ion detection in liquid media at milimolar concentration levels.

A surface acoustic wave (SAW) device contains patterned electrodes on the top piezoelectric substrate. Even though different SAW device configurations have been used, since its discovery by Lord Rayleigh in 1885, the use of interdigital electrodes (IDEs) or interdigital transducers (IDTs) and reflectors by White and Voltmer in 1965 and Staples et al. in 1974, respectively have proven to minimize the power dissipation and hence obtain optimized SAW generation and detection. Several advantageous features such as small size, high resonant frequency, low power consumption and compatibility with CMOS technology, makes them an appropriate choice when compared to conventional sensing systems.

SAW devices have been typically used in the Rayleigh, Lamb, shear horizontal (SH-SAW) and Love propagation modes. In the Rayleigh propagation mode, particle displacement
has two components: one is parallel to the SAW propagation direction and the other is normal to the substrate, thus forming an elliptical trajectory for the particle. Most of the SAW energy is confined to the surface of the substrate and is often diminished to zero at a substrate depth of 4 to 5 times the wavelength. Due to the normal component of the particle displacement and interference with other media, above the substrate surface, this mode is not suitable for a liquid environment.

The Lamb wave is similar to the Rayleigh wave and are typically generated using very thin substrates that are only a few wavelengths thick. Like the Rayleigh waves, Lamb waves have both normal and shear components and can be used for gas sensing, but they are also well-suited for liquid sensing. Due to the low phase velocity of Lamb waves, there is no energy penetration inside liquid media placed on the SAW surface, and hence no acoustic streaming.

On the other hand, in the SH-SAW propagation mode, the particle displacement happens only in parallel with the substrate surface, which prevents the vibration vector from transferring into any secondary media and hence prohibits SAW energy attenuation when the substrate comes into contact with a liquid. Knodoh et al. proved SH-SAW liquid sensing system’s capability by detecting various types of Japanese tea. The liquid properties were evaluated by monitoring the frequency shift and amplitude change of the SH-SAW sensor output. SH-SAW sensor, has also been used for investigating oil contamination of ground water by detecting hydrocarbons in micro molar concentration levels. The use of the SH-SAW device is thus a promising solution for heavy metal compound detection in liquid environments.

Often, a thin-film called a guiding layer is applied to the surface of the device to activate a Love wave mode, which also inhibits radiation of acoustic pressure into the liquid making Love wave operation the most common for sensing in liquids.
Devices that can generate SH-SAWs, with much less bulk leakage, began to appear in the 1990s, and often use a Love thin-film wave guide to further prevent leakage into a liquid on the surface.\textsuperscript{44,45,46,47}

The SAW device is operated at a designed resonant (or center) frequency ($f$) imposed by the IDE design, wherein a typical IDE the electrode spacing is an integer multiple or 1/2, 1/3, or 1/4 of the wavelength $\lambda = 2\pi/k$, with $k$ being the wavenumber and wavelengths typically between 0.01 mm to 1.0 mm.

A variety of IDE designs have been implemented to affect both the resonance and the propagation of the SAW. The most basic is a planar design, where the IDE consists of simple linear electrode ‘fingers’ and the interdigitated spacing is consistent for each finger pair, as shown in Figure 2.1.

![Figure 2.1: Schematic of a planar IDE design SAW device\textsuperscript{48}.](image1)

![Figure 2.2: Curved IDE designed SAW device\textsuperscript{49}.](image2)
However, other clever IDE designs are possible, such as curved or focused IDE (Figure 2.2) configurations to produce focused SAWs\textsuperscript{50} or variable-spacing ‘chirped’ IDEs that produce multiple resonant frequencies.\textsuperscript{51}

A single IDE design is generally used to generate planar traveling waves that propagate along the surface of the device, called a traveling wave, but sets of two or more opposing IDEs can also be used to set up constructive interference and produce standing surface waves. To inhibit reflections and scattering off the edges of the SAW substrate and minimize wave reflection interference, acoustic absorbents such as gels (e.g. alpha gel) are often applied to the edges of the piezoelectric substrate.\textsuperscript{52}

Ultimately, the IDE design depends heavily on the nature of the SAW device and the application in question. The progress in SAW device fabrication methods have focused on developing novel flexible substrates instead of conventional, rigid single-crystal piezoelectric substrates. Jin \textit{et al.} developed flexible SAW devices which operate in Rayleigh and Lamb wave propagation mode by depositing ZnO nanocrystals on bendable Kapton polyimide films.\textsuperscript{53}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{flexible_saw_device.png}
\caption{Flexible SAW device fabricated on a nanocrystal film\textsuperscript{54}.}
\end{figure}
2.3 Fluid Manipulation Techniques for Spray Generation

Spray technologies for the atomization of fluids play an important role across a vast range of technologies ranging from drug delivery and chemical analysis to combustion systems and material coatings. In the biomedical field, aerosolized drug delivery for cystic fibrosis, pneumonia, influenza, respiratory tract infections and pulmonary aspergillus have been under clinical trials. The results illustrate the controllable and concentrated drug delivery in targeted regions which positively affects the dosing and duration of the therapeutic procedures. Various mechanisms can be used to atomize fluids including pneumatic, acoustic and electrically-driven sprays.

2.3.1 Pneumatic Sprays

Pneumatic sprays work based on the interaction of two fluid phases, gas and liquid. Compressed and high velocity gas is pressurized into a liquid jet to produce the spray. These types of atomizers are able to produce the spray out of viscous materials at high throughput, which makes them a subject of interest in painting, air brushes and fuel combustion systems.

This atomizer structure can be designed to be simple and cost effective. However, there is no precise control over the resultant aerosol size and hence the thickness and uniformity of the covered area. The characteristics of the spray are drastically affected by the size, geometry and location of the liquid nozzle.

2.3.2 Acoustic Based Sprays

After Wood and Loomis made the first acoustic based spray system in 1927, Sollner explained that the mechanical vibration of the surface causes the cavitation beneath the surface of the liquid, which results in mist formation. Lang showed that when an ultrasonic transducer
bridges between liquid and air, generated acoustic waves produce capillary waves that are able
to atomize the liquid\textsuperscript{73}. Since then, ultrasonic atomizers have been used for a variety of
applications such as plastics, coatings or in more advanced spray production system designs,
for organic film deposition\textsuperscript{74,75}.

Piezoelectric crystals convert the electrical signal to mechanical vibrations; hence they
are apt choices for this approach. Surface acoustic wave (SAW) devices, explained in part
2.2.2.3, are well-known spray generation techniques. The delivered electrical signal to the
SAW device converts to particle displacement and vibrations due to the piezoelectric features
of the substrate. A sufficient amount of the input electrical signal can initiate particle
displacement in the axis normal to the surface; big enough to leak the energy into the droplet
or liquid film placed on the substrate, as shown in Figure 2.4(a).

![Figure 2.4: (a) Overcoming the surface tension to break the droplet in SAW devices. (b) SAW device configurations\textsuperscript{76}.](image)
The pressure difference and induced capillary wave can destabilize the liquid surface and overcome the surface tension at a specific threshold to break the liquid into atomized droplets. In a typical SAW device, this threshold can be achieved by delivering around 100 V amplitude sinusoidal input voltage\textsuperscript{77}.

SAW based spray generation has been used and available since 1990.\textsuperscript{78,79,80} The physical mechanism behind the spray generation and the designing optimization for SAW atomizer have been well documented in the literatures.\textsuperscript{81,82,83}

Friend, Yeo and collaborators published several papers about the use of microscale aerosolized droplets generated by SAW devices in pharmaceutical\textsuperscript{84} and chemical\textsuperscript{85} industries. It was also demonstrated that the resonant frequency of the SAW device and the geometrical configuration of the interdigital electrodes (IDEs), shown in Figure 2.4(b), can affect the size of the droplets, the uniformity of the mist and the onset voltage for atomization that is achievable by SAW device design and fabrication\textsuperscript{86}.

The resonant frequency of the SAW device is a function of the width of the metalized IDEs patterned on the piezoelectric substrate, calculated by\textsuperscript{87}

\[
f \propto \frac{1}{4w} \quad (2.1)
\]

where \(w\) is the width of the IDE. The radius (\(R\)) of the generated aerosol using the SAW atomizer, on the other hand, this is\textsuperscript{88}

\[
f \propto \frac{1}{R} \quad (2.2)
\]

Therefore, a fabricated SAW device with high center frequencies (in the MHz range) can produce relatively small and mono-dispersed atomized droplets. For atomization applications, the shape of the IDEs can play a major role on the minimum required input voltage, known as onset voltage. This is because patterning specific IDE configurations will enable the acoustic power to be focused on a desired point of the substrate\textsuperscript{89}. However, SAW
device fabrication means patterning micron size metalized fingers on the piezoelectric substrate in a clean room, which can be complicated, time consuming and expensive.

2.3.3 Electrically-Driven Sprays

Electrically-driven sprays, where a high voltage is applied to a liquid flow or film, have a long and distinguished history\textsuperscript{90,91}. To this day, electrosprays are widely used for mass spectrometry systems\textsuperscript{92} and emerging applications include micro-propulsion\textsuperscript{93}, spray coating\textsuperscript{94}, materials synthesis\textsuperscript{95} and printing\textsuperscript{96}.

In electrosprays, positive and negative ions get separated by the electrical field. In the late 16\textsuperscript{th} century, William Gilbert discovered the effect of the electrical field on water droplets, and in the mid-20\textsuperscript{th} century, Sir Geoffrey Ingram Taylor modeled the shape of the cone made by applying the electrical field to the droplets\textsuperscript{97}. A high voltage between 1 to 20 kV is applied between a nozzle electrode and a flat grounded electrode (Figure 2.5). The liquid is provided continually to the nozzle electrode and a substrate is placed on the grounded electrode for thin film formation. When the input voltage, applied to the liquid in the nozzle electrode, crosses the threshold, the liquid is drawn into a cone. The liquid reaching the nozzle electrode tip forms a Taylor cone, which emits a liquid jet through its apex due to charge accumulation at the apex of the cone which overcomes the surface tension of the liquid.

In fact, Taylor cones are the result of the electrified interface between the conductive liquid and air, when the charge reaches a critical level. Initially, a 100 \( \mu \text{m} \) size thin liquid jet and eventually a series of small and highly charged liquid droplets will be formed. The droplet diameter is directly proportional to liquid mass density and indirectly proportional with liquid conductivity and surface tension\textsuperscript{98}. One limitation of most electrospray systems is the nature of the droplet plume, which typically arises from the tip of a liquid cone (Taylor cone\textsuperscript{99} or cone-
jet\textsuperscript{100} and spreads conically to cover an area\textsuperscript{101}. Thus, the projected area of the droplet plume is circular, which is not ideal for applications such as uniform coating.

![Schematic of a typical electrospray system](image)

**Figure 2.5:** Schematic of a typical electrospray system\textsuperscript{102}. High voltage applied between the metal nozzle electrode and substrate generates the spray from the precursor liquid delivered by the syringe.

The size of this plume can be affected by the spray and solution conditions\textsuperscript{103}. Alternative strategies, such as using alternating current (AC) fields, can also be used to generate linear jets of droplets rather than plumes\textsuperscript{104}. Yet, developing ways to generate a uniform, broad area droplet plume could be important for applications such as spray coating.

As another type of electrically-driven spray formation, paper spray is an ambient ionization method that is well known as a reliable, time efficient, easy way for mass spectrometry with no sample preparation\textsuperscript{105}. Similar to electrospray ionization, it appears to produce charged droplets via Taylor cones. Typically, 3-5 kV input voltage is required and applied to a piece of paper which contains the desired liquid, via copper clips to make the spray out of the liquid as shown in Figure 2.6\textsuperscript{106}. Delivering a sufficient electrical field will produce charged droplets by liquid breakage due to Columbic forces according to\textsuperscript{107}

\[ F = \frac{V}{r} \] (2.3)
where $V$ is the applied voltage and $r$ is the radius of the cut paper knowing that the minimum necessary field strength for field ionization which is around $10^7 \text{ V cm}^{-1}$.

For this purpose, various types of papers, ranging from chromatographic paper to fiber glass papers, have been cut to have a sharp point with a tip angle between $60^\circ$ to $150^\circ$ and used for paper spray\textsuperscript{108}. Research has shown that fiber glass paper shows poor performance when compared to chromatographic papers\textsuperscript{109}. The sharp tip of the paper can provide a higher electric field as well as help in microfluidic transportation\textsuperscript{110}. High resolution images and phase Doppler analysis have demonstrated the mechanism behind paper spray ionization by Espy et al.\textsuperscript{107}. High speed photographic images suggested this phenomenon occurs in two separate modes depending on the solvent flow rate. Taylor cones are formed and numbered in the (Figure 2.7). The first mode happens for high solvent flow rates by applying 3.5 to 4.5 kV and 0.1 to 0.2 $\mu$A, where Taylor cones result in a wide range of droplet size formations. After a sufficient amount of solvent is depleted, mode two will occur. In this mode, the solvent flowrate is smaller and the current is higher when compared with the first mode; also, corona discharge generates smaller and monodispersed droplets. The short spitting mode in paper spray makes it a proper method for mass spectrometry but not practical in procedures that needs a longer endurance such as coating applications.
This chapter provided a brief background and introduction to fluid manipulation in sensing and spray generation systems. The conventional systems for sensing toxic heavy metal ions in liquid media were introduced. The conventional sensing systems are expensive, time consuming and need complicated procedures with trained staff which suggests introducing a new procedure that overcomes these drawbacks. Spray generation technologies were also
summarized in this chapter. Based on the high applied voltage, small area coverage and non-continuity of the spray generated by the conventional systems, this field of study still needs an innovative idea that overcomes these deficiencies. The author will discuss how piezoelectric devices can be a proper choice to design new systems for sensing and spray generation techniques that conquer the obstacles of the traditional approaches.

2.5 References


CHAPTER III

INVESTIGATION OF A PIEZOELECTRIC BASED SENSOR FOR TOXIC HEAVY METAL DETECTION

3.1 Introduction

Some of the most common heavy metal pollutants are lead (Pb) and cadmium (Cd). Pb has been categorized as a neurotoxic element due to its severe impact on the nervous system, causing neurotoxicity and nephrotoxicity in the gastrointestinal and renal systems. Cd, which has been increasingly used in industrial product lines, is known to cause kidney failure, hypercalciuria and osteoporosis. Mercury (Hg) is the second most toxic heavy metal in the planet. Hg is a neurotoxicant, which targets the central nervous system as well as liver and heart muscles in the human body. Nickel (Ni) has been seeing a rising demand in the surface coating and jewelry industries. Ni is a carcinogenic contaminant, which causes pulmonary fibrosis, asthma, lung and nasal cancer in case of long term exposures. All these elements are often released from natural and manmade sources and have the capability to accumulate in the vital organs and cause fatalities.

Heavy metal detection methods including spectrometric techniques such as cold vapor atomic absorption spectroscopy, inductively coupled plasma mass spectroscopy, electrochemical impedance spectroscopy, UV-visible absorbance spectroscopy, x-ray, laser and colorimetric analysis as well as biosensing detection techniques based on enzyme activation or bacteria have been reported. However, these techniques are often expensive, time consuming, laborious, hazardous and require complex labeling methods.
Therefore, it is necessary to develop sensing systems with easy-to-use, cost effective, highly sensitive and rapid detection techniques.

In this work, the author has designed and fabricated an efficient piezoelectric device, consisting of gold (Au) interdigital electrodes (IDEs) on a 64° YX-LiNbO₃ based piezoelectric substrate known as a shear horizontal surface acoustic wave (SH-SAW) sensor, for the detection of heavy metal compounds. The main focus of the author was to design a system which has a small limit of the detection to be able to show a recordable signal for low concentrations of the toxic heavy metals in liquid media. The range of the detected heavy metals by this system was desired to be as wide as possible. Proper chemical sensing layer, Phenol or naphtho[2,3-a]dipyrido[3,2-h:2',3'-f]phenazine-5,18-dione (QDPPZ) are used to selectively bind to the heavy metal ions. An acrylic based flow cell was used to hold the sensor and PDMS microfluidic channel. The capability of the system for detecting different concentrations of heavy metal compounds, such as lead nitrate (PbNO₃), cadmium nitrate (CdNO₃), mercury (II) nitrate, (Hg(NO₃)₂) and nickel (II) nitrate (Ni(NO₃)₂) in liquid environments, through phase shifts in the frequency based response (S₂₁) of the SH-SAW sensor are investigated.

3.2 Theory

For sensing applications, the SAW devices typically work at higher frequencies (~100-500 MHz) whereas most microfluidic devices operate at lower frequencies (~10-100 MHz). The most common piezoelectric substrates are single crystal lithium niobate (LiNbO₃), lithium tantalate (LiTaO₃), and quartz (SiO₂) with common cuts including 128° y-x cut for LiNbO₃ and ST and AT cuts for quartz substrates.

The piezoelectric based SH-SAW devices, generally consists of two sets of metalized input and output IDEs mounted on a piezoelectric substrate. The surface acoustic wave is
generated by an impulse or sinusoidal input electrical signal applied at the input IDEs. It then propagates on the piezoelectric substrate through the delay line, which is the distance between the input and output IDEs and is converted back to an electrical signal, as shown in Figure 3.11.

![Figure 3.1: Schematic of a delay line SAW device with input and output IDEs.](image)

The SH-SAW device output signal can finally be obtained from the output IDEs. The SAW resonant frequency can be mathematically calculated by\(^{21}\)

\[
\begin{align*}
  f_0 &= \frac{v_s}{\lambda} \\
  \lambda &= 4 \times w
\end{align*}
\]

where, \(f_0\) is the resonant frequency of the SAW, \(v_s\) is the SAW propagation velocity on the piezoelectric substrate, \(\lambda\) is the SAW wavelength and \(w\) is the width of the IDEs. The resonant frequency of the SH-SAW sensor is dependent on the velocity of the acoustic wave passing through the piezoelectric substrate. The velocity of the wave is known to vary due to mass, stiffness, conductivity, dielectric coefficient, temperature and pressure changes\(^{22}\). The absorbance of the different concentrations of toxic heavy metals by the sensitive layers, which are coated on top of the piezoelectric substrate, causes a mass loading effect to take place. mass loading also changes the SAW propagation velocity and thus the resultant center frequency, which can be used to quantify the concentration levels\(^{23}\).
The principle behind SAW-based sensing devices is that the target chemicals that adsorb on a functionalized surface on the SAW substrate fundamentally change the frequency of the SAW, and measurement of the frequency shift ($\Delta f$) can be correlated to the concentration of the target species. Based on this principle, SAW sensors were initially developed more than three decades ago$^{24,25}$, and are currently employed as fundamental components in a variety of microsensing systems.$^{26}$ The main advantage associated with SAW sensors is their high sensitivity and capability for the trace detection of a wide variety of chemical materials including bio/chemicals$^{27,28}$, organic and inorganic vapors$^{29,30}$, and explosives.$^{31}$

Chemical SAW sensing systems utilize a sensing layer on the SAW substrate that is designed to react or bind with the analytical target. The sensing layer interacts with the target to cause detectable changes in the features of the acoustic wave, such as the velocity or amplitude, which are then manifested as a frequency shift or insertion loss.

According to the literature, increasing the resonant frequency can enhance the sensor performance by increasing the amount of the frequency shift response to the change in media and subsequent sensitivity. However, at frequencies in the GHz range, the noise factor will have more effect on the results. The sensitivity of the sensor is defined as$^{32}$

$$S = \frac{\Delta f}{f_0} \frac{f_0}{u}$$  \hspace{1cm} (3.3)

where the $\Delta f$ is the frequency shift of a sensor with resonant frequency equal to $f_0$ in response to the unit measurand of $u$. 

41
3.3 Experimental

3.3.1 Chemicals, Materials and Sample Preparation

PbNO₃, CdNO₃, Hg(NO₃)₂ and Ni(NO₃)₂ in crystalline form, were purchased from the Sigma Aldrich Chemical Company. Various solutions of deionized water and PbNO₃, CdNO₃, Hg(NO₃)₂ and Ni(NO₃)₂ in concentrations of 1 pM, 100 pM, 1 nM, 100 nM, 1 µM, 50 µM, 100 µM and 750 µM were prepared. PbNO₃, CdNO₃, Hg(NO₃)₂ and Ni(NO₃)₂ are all soluble in the DI water and the process will not be affected by NO₃⁻ anions. All test analytes were stored at −20 °C in 10 ml aliquots before use. Tubing (Inner diameter - 0.01"; Outer diameter – 0.0625") and tube connection accessories for sample transfer were purchased from Upchurch Scientific.

3.3.2 Synthesis of the Chemical Sensing Layer

The sensitive layer for this experiment, which has been synthesized for sensing applications, was acquired from the Chemistry Department at Western Michigan University. The chemical sensing layer QDPPZ was synthesized using a two-step process. In the first step, concentrated sulfuric acid (H₂SO₄, 20 mL) and concentrated nitric acid (HNO₃, 10 mL) were added dropwise to a mixture of 1,10-phenanthroline (1.00 g, 5.56 mmol) in the presence of potassium bromide (KBr) (5.95 g, 50 mmol) at 0°C. The solution was refluxed for 2 hours then cooled to room temperature, yielding a black, oily product. The contents of the flask were diluted with 400 ml deionized water and neutralized with sodium bicarbonate (NaHCO₃), yielding a clear yellow solution. The product was extracted with methylene chloride and dried over anhydrous magnesium sulfate (MgSO₄). The solvents were removed using a rotary evaporator, resulting in a yellow solid. The product was purified by
recrystallization from methanol. The average yield of the product, 1,10-phenanthroline-5,6-dione was (1.11 g, 5.31 mmol) which was calculated to be 95%. The resulting material was achieved to be formulated as 1H NMR (400 MHz, CdCl₃, 25 °C) δ: 9.12-9.10 (t, 2H, J = 2.95 Hz), 8.51-8.48 (d, 2H, J = 1.83 Hz), 7.60-7.55 (m, 2H, J = 4.71 Hz).

In the second step, 1,10-phenanthroline-5,6-dione (0.50 g, 2.38 mmol) was refluxed in ethanol for 15 min. 9,10-diaminoanthroquinone (0.981 g, 2.38 mmol) was then added, resulting in a purple solution, and the solution was refluxed for 4 hours. The dark purple product was collected using vacuum filtration, washed with methanol and concentrated in vacuum. The reaction yield was 80%. Resulting material was achieved to be formulated as 1H NMR (400 MHz, CdCl₃, 25 °C): δ 9.83 (d, 1H), 9.64 (d, 1H), 9.28 (d, 2H), 8.64 (dd, 2H), 8.27 (q, 2H), 7.82 (m, 4H). The final structure is shown in Figure 3.

![Figure 3.2: Structure of QDPPZ.](image)

### 3.3.3 Sensor Fabrication

Figure 3.3(a) illustrates the schematic of the SH-SAW device. The SH-SAW sensor was fabricated on a 64° YX-LiNbO₃ piezoelectric substrate using photolithography techniques. Eight pairs of input and output IDEs, 0.1 μm thick Au, were patterned by metal sputtering
technique on the piezoelectric substrate. The electrode aperture is 760 µm, while electrode width and gap are 10 µm thereby resulting in a 40 µm acoustic wave length (λ). The SH-SAW sensor also consists of 120 reflectors fabricated on the outer side of the input and output IDEs with similar dimensions and 20 reflectors in between the IDEs to reduce the scattering losses of surface acoustic waves. Since the SAW propagation velocity on the 64° YX-LiNbO₃ piezoelectric substrate is 4474 m/s and the designed wavelength is 40 µm, the resultant resonant frequency is calculated to be 111.8 MHz. The photograph of the fabricated SH-SAW sensor, with overall device dimensions of 11 × 12 mm² is shown in Figure 3.3(b). Two sets of input IDE, output IDE, reflectors and electrical pads were patterned on one substrate for cost efficiency purposes. Author just used one set for this experiment.

Figure 3.3:(a) Schematic of the SH-SAW device and (b) fabricated SH-SAW sensor.
3.3.4 Flow Cell Fabrication

The flow cell for this experiment was provided by the Sensor Technology Laboratory (STL) in the Electrical and Computer Engineering Department at Western Michigan University. The flow cell, with overall device dimension of $70 \times 50 \times 52$ mm (w/l/h), was designed in AutoCAD™ and CNC machined using acrylic material (Figure 3.4). A microfluidic flow channel, with dimensions of $710 \times 6800 \times 710$ µm (w/l/h) and a total channel volume of approximately $3.4$ µl, was also fabricated with PDMS. The flow of the test analyte through the PDMS microfluidic channel was obtained by integrating two sets of inlet and outlet ports in the flow cell.

![Flow Cell Diagram](image)

**Figure 3.4: Flow cell with the SH-SAW sensor in the sensor groove (Inset: PDMS microfluidic flow channel).**

The effective closing of the flow cell, which results in the tight sealing of the PDMS microfluidic flow channel around the sensing area of the SH-SAW sensor, was made possible by the use of an axially magnetized set of neodymium magnets (Diameter - 0.25”; Thickness - 0.375”; Magnetic strength – 13,200 Gauss) purchased from K&J Magnets, Inc.
3.3.5 Experiment Setup

The experiment setup is shown in Figure 3.5. The SH-SAW sensor was placed in the sensor groove of the flow cell. Calibration for the wires and probes was done before the measurements. Before use and at the end of each experiment, the sensor was cleaned with acetone, and then blow dried with pressurized air. The measurements were performed at constant room temperature (25 °C), using a heater occupied with thermocouple, since any changes in the temperature would affect the SAW velocity and attenuation.\(^{40}\)

Initially, a reference signal for deionized (DI) water was obtained. Then varying concentrations of analytes were injected into the flow cell using a KD Scientific (KDS210P) programmable syringe pump, at a flow rate of 50 μL/min. An Agilent 4395A network analyzer was used to measure the frequency response (\(S_{21}\)) of the SH-SAW sensor towards the test analytes. System control, data acquisition and post processing of the network analyzer measurements was performed using a LabView\textsuperscript{TM} based application.

![Figure 3.5: Experimental setup.](image)

3.4 Results

To investigate the practicality of the system, results were first obtained towards different concentrations of Pb(NO\(_3\))\(_2\). Figure 3.6 shows the frequency response (\(S_{21}\)) of the SH-SAW measured using network analyzer which contains both magnitude or insertion loss and
phase. The author decided to record the phase aspect of the frequency response since it results in an easier to detect shift.

![Figure 3.6: Magnitude (insertion loss) and phase of the frequency response for SH-SAW sensor.](image)

Figure 3.7 shows the frequency response ($S_{21}$) of the SH-SAW towards different concentrations of PbNO$_3$. It was observed that the resonant frequency of the reference signal established by DI water shifted from 108.564 MHz to 108.551 MHz, 108.543 MHz, 108.529 MHz, 108.508 MHz, 108.503 MHz, 108.499 MHz, 108.494 MHz and 108.479 MHz for the 1 pM, 100 pM, 1 nM, 100 nM, 1 μM, 50 μM, 100 μM and 750 μM concentrations of PbNO$_3$ solution, respectively (Figure 3.7 (a)). This results in frequency shifts of 13 kHz, 21 kHz, 35 kHz, 56 kHz, 61 kHz, 65 kHz, 70 kHz and 85 kHz along with percentage changes of 0.011 %, 0.019 %, 0.032 %, 0.051 %, 0.056 %, 0.059 %, 0.064 % and 0.078 % for the 1 pM, 100 pM, 1 nM, 100 nM, 1 μM, 50 μM, 100 μM and 750 μM concentrations of PbNO$_3$ solution, respectively when compared with DI water (Figure 3.7 (b)). The experiment was repeated
seven times using two different fabricated sensors and standard deviations of 3.5 kHz, 1.7 kHz, 2.1 kHz, 6.8 kHz, 3.5 kHz, 4.6 kHz, 2.1 kHz and 5.6 kHz from the average value of 15 kHz, 22 kHz, 33 kHz, 48 kHz, 57 kHz, 64 kHz, 69 kHz and 80 kHz were achieved for the 1 pM, 100 pM, 1 nM, 100 nM, 1 μM, 50 μM, 100 μM and 750 μM concentrations of PbNO₃ solution, respectively.

Figure 3.7: (a) SH-SAW sensor frequency response (S₂₁) based on phase variation towards varying concentrations of PbNO₃ and (b) Changes in frequency shift of SH-SAW sensor response.

Then, varying concentrations of CdNO₃ were injected onto the SH-SAW sensor. It was observed that the resonant frequency of the reference signal established by DI water shifted from 109.290 MHz to 109.100 MHz, 109.076 MHz, 108.989 MHz, 108.979 MHz,
108.963 MHz, 108.948 MHz, 108.944 MHz, 108.935 MHz and 108.933 MHz for the 1 pM, 100 pM, 1 nM, 100 nM, 1 μM, 50 μM 100 μM, 250 μM and 750 μM concentrations of CdNO$_3$ solution, respectively. The frequency response ($S_{21}$) of the SH-SAW sensor demonstrated frequency shifts of 190 kHz, 214 kHz, 301 kHz, 311 kHz, 327 kHz, 342 kHz, 346 kHz, 355 kHz and 357 kHz along with percentage changes of 0.173 %, 0.195 %, 0.275 %, 0.284 %, 0.299 %, 0.312 %, 0.316 %, 0.324 % and 0.326 % for the 1 pM, 100 pM, 1 nM, 100 nM, 1 μM, 50 μM 100 μM, 250 μM and 750 μM concentrations of CdNO$_3$ solution, respectively when compared with DI water (Figure 3.8). The experiment was repeated eight times using two different fabricated sensors and standard deviations of 4.2 kHz, 1.1 kHz, 1.1313 kHz, 1.6 kHz, 1.7 kHz, 2.5 kHz, 1.6 kHz, 1.5 kHz and 1.3 kHz were obtained from the average value of 109 kHz, 129 kHz, 175 kHz, 192 kHz, 203 kHz, 217 kHz, 221 kHz, 235 kHz and 271 kHz for the 1 pM, 100 pM, 1 nM, 100 nM, 1 μM, 50 μM 100 μM, 250 μM and 750 μM concentrations of CdNO$_3$ solution, respectively.

Also, Figure 3.9 shows the SH-SAW sensor resonant frequency shift for the varying concentrations of Ni(NO$_3$)$_2$ solution, when compared with DI water. Frequency shifts of 273.3±60 kHz, 441.7±50 kHz, 566.7±49 kHz, 673.3±43 kHz and 806.7±57 kHz was observed for the 1 pM, 100 pM, 1 nM, 100 nM and 1 μM concentrations of Ni(NO$_3$)$_2$ solution, respectively.
The resonant frequency shifts can be attributed to the change in SAW propagation velocity, in the delay line, caused by the varying concentrations of the test analytes. The development of a selective and sensitive chemical sensing layer relied on the deposition of the organic ligand, QDPPZ, which is a 1,10-phenanthroline derivative that consists of nitrogen and oxygen groups that will coordinate to attach the heavy metal ions. Initial work has demonstrated that the quinolone unit was essential in inducing selectivity towards the heavy metal ions, which was not observed if 1,10-phenanthroline alone was used. The binding of
QDPPZ to the heavy metal ions causes an increase in mass between the electrodes, thus affecting the surface acoustic wave function. As the ions flow through the sample channels, QDPPZ molecules coordinate with the metal ions, forming a complex and increasing the mass of the material between the electrodes.

However, QDPPZ was not an apt choice for mercury ion detection. Performing the same experiment using mercury nitrate did not show any frequency shift in our SAW sensing system. This suggested that unlike lead, cadmium and nickel, QDPPZ is not an adsorbent for mercury ions. In the second attempt for mercury nitrate detection using our system, the author used Phenol as the sensing layer on the SAW sensor, based on the approved binding event between phenolic group and metals such as copper\textsuperscript{41}, and the ability of the system towards the mercury nitrate detection was tested by introducing different concentration of Hg(NO\textsubscript{3})\textsubscript{2} solution.

Figure 3.10 shows the SH-SAW sensor resonant frequency shift for the varying concentrations of Hg(NO\textsubscript{3})\textsubscript{2} solution, when compared with DI water. Frequency shifts of 184.8±23 kHz, 378.3±62 kHz, 458.3±80 kHz, 600.0±96 kHz and 748.3±116 kHz were observed for the 1 pM, 100 pM, 1 nM, 100 nM and 1 μM concentrations of Hg(NO\textsubscript{3})\textsubscript{2} solution, respectively.

![Figure 3.10: SH-SAW sensor frequency shift towards varying concentrations of Hg(NO\textsubscript{3})\textsubscript{2}.](image)
These sets of frequency responses also displayed detection levels as low as picomolar concentrations and the ability of this piezoelectric sensor to distinguish among a wide range (micro, nano and pico level) of sample concentrations. The results satisfied the main goal of this chapter which was introducing a sensing system with a small limit of detection.

The results obtained demonstrated that phenol and QDPPZ can be employed as sensitive layers for Hg(NO₃)₂ and PbNO₃, CdNO₃ and Ni(NO₃)₂, respectively. It is worth noting that the approved toxicity level of Pb and Cd according to the United States Food and Drug Administration (USFDA) is 1.25 mM and 207 µM, respectively. The United States Environmental Protection Agency (EPA) reported maximum allowable level for Hg(NO₃)₂ and Ni(NO₃)₂ in drinking water to be 10 nM and 0.3 µM, respectively. Considering these toxicity limits, this system can follow any trace of these toxic heavy metals before the toxicity reaches to the dangerous level to avoid any health issues.

3.5 Summary

In this chapter, the author provided a brief introduction about the conventional methods of toxic heavy metal detection in aqueous solution as well as the needs of improving these methods. The author then described theoretical explanations of the piezoelectric sensing based system. This was followed by a detailed report of the performed experiments including the chemicals, materials and sample preparation; synthesis of the chemical sensing layer; sensor fabrication; flow cell fabrication and experiment setup. Final results of the experiments are also represented.

To summarize, a SH-SAW sensor was successfully fabricated on a 64° YX-LiNbO₃ piezoelectric substrate. An efficient flow cell was also designed and fabricated using acrylic material. The flow cell consisted of inlet and outlet ports for the microfluidic chamber and PDMS based microfluidic channels. The feasibility of using the SH-SAW sensor for detecting
heavy metal compounds was demonstrated through the quantitative detection of PbNO₃, CdNO₃, Ni(NO₃)₂ and Hg(NO₃)₂. A proper chemical adsorbent was used as the sensing layer.

The measured resonant frequency response shift of the SH-SAW sensor demonstrated a 13 kHz, 190 kHz, 273 kHz and 184 kHz frequency shift for the 1 pM concentrations of PbNO₃, CdNO₃, Ni(NO₃)₂ and Hg(NO₃)₂ respectively, when compared with the DI water. The results show the capability of the SH-SAW sensor to detect pico molar concentrations of toxic heavy metals in water, which is several orders of magnitude lower than the maximum allowable level for toxicity in drinking water.

3.6 References


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CHAPTER IV

PIEZOELECTRIC TRANSFORMER BASED SPRAY GENERATION SYSTEM

4.1 Introduction

The drawbacks of the conventional spray generation systems, were discussed in detail in the literature review (Section 2.2), including the lack of thickness and uniformity control in pneumatic sprays, the time and money consuming fabrication process of surface acoustic devices in acoustic spray systems, and applied high applied voltage and the plum shaped spray area in electro sprays. These challenges indicate the necessity of further research and system design in this area of this technology. In this chapter, the author has been investigating the ability of piezoelectric crystals, in a simple and reliable design, significantly improve spray generation.

In this study, the author utilized a piezoelectric transformer for inducing the generation of a broad area electrospray. A piezoelectric transformer (PT) is a piezoelectric device that directly amplifies a low input alternating current (AC) voltage (~10 V) to values that are several orders of magnitude larger (~10^2-10^3 V) through the electromechanical coupling effect of the piezoelectric substrate.

The physics underlying the generation of this spray are complex, and the exact mechanism is unclear. It is well known that the PT generates both mechanical displacement (vibration) and high surface voltages (with accompanying electric field) at the end of the crystal where it is in contact with a paper wick. It has been previously demonstrated that ultrasonic
piezoelectric actuation can be used to vibrationally break a liquid film and atomize liquid on the surface. Furthermore, on 128°YX LiNbO₃ crystals, both surface acoustic Rayleigh and Lamb waves have been shown to atomize fluid on the surface, although at radio frequencies (~MHz) much higher than those used here.

In this chapter, the author introduces a novel approach of broad spray formation using a piezoelectric transformer (PT). A 100 mm × 15 mm × 0.5 mm (l/w/t) 128°YX LiNbO₃ piezoelectric crystal PT device was used at the second resonant frequency. Using a rectangular micro fiber glass paper, liquid film was delivered to the crystal surface. Applying the AC voltage at the resonant frequency led to the liquid film break down and spray formation along the entire width of the PT device. A comprehensive study was performed by the author to investigate the mechanism and the effect of parameters such as liquid properties or power delivery on the spray formation.

4.2 Experiments and Results

4.2.1 Piezoelectric Transformer and Stand Design

A 100 mm × 15 mm 5 mm (l/w/t) cut of a piezoelectric crystal was used as the piezoelectric (PT) device. Although different geometric configurations can be used, the author utilizes one that is based on a linear 128°Y-cut lithium niobate (LiNbO₃) crystal. Bottom and top electrodes were formed by painting silver electrodes half the length of the PT on both sides. A proper stand was designed using AutoCAD software and 3D printed to hold the PT in a location that support the second resonance standing wave nodes (Figure 4.1).
The PT was actuated by a signal generator (Agilent Model 33220A) connected to an RF amplifier (Powertrone Model 500A). Sinusoidal waveforms were used for the studies. An oscilloscope (Tektronix DPO 2024B) was used to measure the applied voltage and current via a resistor-capacitor-inductor (RLC) notch filter set at the driving frequency. A PT-driven electrospray was generated by applying an AC input voltage, at the second harmonic resonant frequency of the 128°YX LiNbO$_3$ crystal, to two electrodes on the top and bottom of the piezoelectric surface. The resonant frequency is a strong function of the surrounding capacitance of the system, and for these studies, the second resonance was typically ~60 kHz.

### 4.2.2 Spray Generation

To generate the spray, various deionized (DI) water based aqueous solutions were filled in an adjacent reservoir and a paper wick was placed in the reservoir and in contact with the surface of the PT, as shown in Figure 4.2(a). The paper bridge serves to continuously wick the solution to the PT surface, allowing the generation of a continuous electrospray, similar to methods used for surface acoustic wave atomization$^5$. Various types of paper were examined.
as the wick, the paper PT contact and spray consistency were each observed. Ultimately, fiberglass paper (Ahlstrom Company) produced the most consistent spray.

As shown in Figure 4.2(b), inputting an AC voltage at one end of the crystal generates a standing mechanical wave, and due to electromechanical coupling, a large polarization is generated along the surface of the crystal. By mounting the crystal, so that the nodal resonance of the standing wave is pinned, substantial surface voltages are reached at the crystal tip.

![Figure 4.2: (a) PT-driven electrospray configuration with solution delivery from a paper wick. (b) Geometric configuration of the PT with resulting standing displacement and stress wave. (c) Photograph of PT-generated electrospray of 50 mM NaCl solution.](image)

Figure 4.2: (a) PT-driven electrospray configuration with solution delivery from a paper wick. (b) Geometric configuration of the PT with resulting standing displacement and stress wave. (c) Photograph of PT-generated electrospray of 50 mM NaCl solution.

Notably, it has been shown that these surface potentials are sufficient to breakdown gas and form a plasma\(^6,7,8\). Here, the author utilizes this surface voltage to generate a continuous electrospray by supplying an aqueous solution to the crystal surface.

Figure 4.2(c) shows an image of a PT-generated electrospray of a sodium chloride solution (50 mM, NaCl) using an input AC voltage amplitude of 15 V\(_{\text{amp}}\) at 59.78 kHz. The author found that the spray forms directly from the paper wick, and only when the wick is in good contact with the PT. Unlike conventional electrospray, there is no secondary or ‘counter’ electrode used here, nor is the liquid actively pumped through a capillary by an external source such as a syringe pump. Instead, liquid flow is driven through a combination of capillary action,
to saturate the paper, and an electrokinetic flow as mass is removed by the spray. Thus, the spray is inherently self-limited by the amount of electrokinetic flow that can be generated. Unlike conventional electrospray, the droplets do not appear to be formed from Taylor cones; rather the behavior is more like a spitting mode\textsuperscript{9}. Also, of note is that, because there is no counter electrode and the field is inherently AC, the droplets leaving the paper are not directed by an electric field as in conventional DC electrospray. Instead, they essentially follow ballistic projectile trajectories under the influence of gravity, falling to the surface beneath the PT. The spray is generated uniformly along the width of the LiNbO\textsubscript{3} crystal, which is 15 mm for these experiments, such that the spray covers a much wider area than the circular area covered by a typical capillary electrospray. This could be especially useful for spray applications to cover a wide area.

### 4.2.3. Spray Coating Profilometry

To demonstrate this spray generation system’s potential for wide area coating purposes, the author sprayed fluorescent microspheres onto a glass slide placed beneath the PT. Figure 4.3(a) shows the 3D profilometry of a glass substrate spray-coated by 1 \( \mu \)m red fluorescing polymer microspheres (Duke Scientific Corp.) diluted in an aqueous solution of 50 mM NaCl. The spray was operated at 20 V\textsubscript{amp} AC input voltage for 70 seconds. The surface roughness of was measured to be 0.05 \( \mu \)m over an area of 15 mm \( \times \) 5 mm using a profilometer (Bruker from Lafayette Instrument Co.). This roughness is negligible when compared with the 1 \( \mu \)m bead diameter, and indicates uniform coating. Figure 4.3(b) provides a scanning electron microscope (SEM) image of the deposited beads, showing fairly uniform coverage.
Figure 4.3: 3D profilometry of a glass slide coated by 1 µm beads. The roughness was determined to be 0.05 µm over an area of 15 mm × 5 mm. (b) SEM image of as deposited particles.

4.2.4 Volumetric Flow Estimation

The author measured the weight (and hence volume) of the collected spray using a digital lab scale as a function of time to estimate the volumetric flow rate. The PT was mounted above the sensitive plate of a precise weight balance (Ohaus Adventurer Pro Digital Balance) connected to a PC and a Matlab-based program for data acquisition (Appendix A). The generated spray was directly collected in a container on the balance, and the weight was averaged over 30 s at a rate of 10 samples/s.
Figure 4.4: Generated spray volume for 5 mM NaCl solution in DI water versus time. The slope of the curve fit indicates a constant volumetric flow rate of 20 µL/min over 5 min of applied constant 19 V<sub>amp</sub> AC input voltage. The dash lines represent the standard deviation in the spray volume from three repeated experiments.

The entire experiment was conducted in a glass box to limit the influence of random drafts in the laboratory and limit the influence of evaporation. Figure 4.4 shows the measured volume as a function of time for a duration of 5 minutes, illustrating the overall stability of the spray.

The author estimated that the volumetric flow rate is ~12-30 µL/min, depending on the exact experimental conditions (input voltage, spray solution). For comparison, most mass spectrometry applications use rates between 0.1-10 µL/min, and most spray coating applications have rates of 10-600 µL/min<sup>10,11</sup>.

### 4.2.5 Linear Flow Speed Visualization

To confirm that the flow was not simply due to capillary action, the author also tracked the solution front through the paper wick using red dye. The pumping effect of the PT-driven spray system was investigated by tracking the flow front of red dye through the paper (Fig. 4.5).
Figure 4.5: Front tracking of the red dye during spray generation.

Using videography, the flow front was visualized and a frame-by-frame analysis was used to analyze the flow.

Figure 4.6 shows the front distance as a function of time, and the linear relationship indicates a constant flow speed of ~0.12 mm/s. In contrast, the distance-time relationship for strict capillary flow is non-linear \((d \sim t^{1/2})\), and the author measured that wicking alone over 10 min caused the front to progress approximately 3 mm. The solution front progresses linearly with time, indicating a constant speed through the paper wick. This evidence indicates that the PT is actively pumping the fluid during the spray process faster than capillary action alone.

Figure 4.6: Distance of the front of red dye through the paper wick as a function of time with applied constant 20 Vamp AC input voltage at 59.91 KHz. The dotted line is a linear curve fit indicating a constant speed.
4.2.6 Bulk Motion of Droplets Directly on the PT Device

To assess whether this phenomenon was similar to other conventional PT based spray formation mechanisms, two 10 ml droplets of DI water were placed on the surface, one near the center and the other at the corner of the PT device as shown in Figure 4.7. Upon application of a 13 V<sub>amp</sub>, 59.9 kHz input, no bulk translation was observed for the droplet that was placed at the center, but the one closer to the corner was translated to the edge of the PT. As shown in Figure 4.7, the droplet subsequently wetted the edge of the PT crystal, however no spray was formed. Further, for droplet volumes as small as 200 nL, no spray was generated and for droplets greater than 15 mL, no bulk motion of the droplet or atomization was observed. This suggests that the mechanism is not vibrational, but rather electrical.

![Image](image.png)

Figure 4.7: Time evolution of droplet motion under a 13 V<sub>amp</sub>, 59.9 kHz input to the PT. The droplet nearest the corner eventually translated to the edge of the PT, wetting it, but no spray was formed. The more central droplet only exhibited vibrational motion, but no bulk translation.

4.2.4 Measurement of Output Voltage

Prior to behavioral studies of this novel approach of spray generation, the author first confirmed that the output voltage was of sufficient magnitude to generate an electrospray.

The output voltage of the transformer is proportional to the applied input voltage, crystal properties, and device geometry. It can be determined using<sup>12</sup>
\[
\frac{V_{\text{out}}}{V_{\text{in}}} \propto k_{23} k_{33} Q \frac{L}{T} \tag{4.1}
\]

where \( V_{\text{in}} \) is the input voltage, \( k_{23} \) and \( k_{33} \) are the transverse and longitudinal vibration coupling coefficients, \( Q \) is the crystal loss factor, and \( L \) and \( T \) are the length and thickness of the crystal, respectively. For a 128° Y-cut \( \text{LiNbO}_3 \) crystal, \( Q \) and the product \( k_{23} k_{33} \) are reported to be approximately \( 10^4 \) and 0.3, respectively\textsuperscript{12}. In these studies, the crystal length is 100 mm and the crystal thickness is 0.5 mm, allowing the voltage gain to be estimated as 1.5\( \times \)10\textsuperscript{5}.

To attempt to confirm this gain, the piezoelectric transformer output voltage was measured via a piece of wire mounted on the tip of the PT and connected to an oscilloscope, as shown in Figure 4.8(a). As shown in the plot (Figure 4.8(b)), the output voltage increases linearly with input voltage, and a curve fit shows a voltage gain of about 124. This is significantly lower than that predicted by Eq. (4.1). However, this can be attributed to the inherent challenge of measuring the output voltage. Discharges tend to form at triple points and the output wire connected to the PT forms such triple points. These discharges, which were observed visually, generated a significant voltage drop, reducing the value measured from the wire itself. Also, the output wire and oscilloscope were changing the load resistance, which was suggesting the replacement of a super conductive wire could increase the measured gain. This experiment, however, does confirm that the gain is at least \( 10^2 \) for this configuration. Thus, even for an input of 10 \( V_{\text{amp}} \), an output voltage of about 1240 V is expected, which is more than sufficient to generate an electrospray.
Figure 4.8: (a) PT output voltage measurement configuration. (b) PT output voltage as a function of the applied input voltage at a frequency of 60 kHz.
4.2.5 Effect of Liquid Conductivity on Spray Current

To explore whether the spray behaves similar to a conventional electrospray, a series of studies were conducted to investigate the effect of the electrical conductivity and surface tension of the solution on spray production. Based on electrospray theory, the author expects to see that the output spray current $i_{spray}$ increases non-linearly with the liquid conductivity and surface tension following

$$i_{spray} \propto (\gamma \lambda_m^0 C)^n$$  \hspace{1cm} (4.2)

where $\gamma$ is the surface tension, $\lambda_m^0$ is the limiting molar conductivity, $C$ is the concentration of the electrolyte, and $n$ is an empirical constant between 0.2 $^{13}$ and 0.5 $^{14}$.

To study the effect of the electrolyte conductivity, aqueous solutions of sodium chloride (NaCl) and hydrochloric acid (HCl) were used for testing due to the considerable difference in their limiting molar conductivity. The limiting molar conductivity of (Na$^+$) in water is $50 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, whereas for H$^+$ it is $350 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, due to the high mobility of the proton$^{13}$.

To study the effect of the conductivity of the liquid on the generated spray current, the output current was measured by placing a grounded collecting electrode beneath the PT connected to a picoammeter and a PC containing a LabVIEW base program for data acquisition and further analysis (Figure 4.9).

![Figure 4.9: PT driven generated spray current measurement configuration.](image-url)
Solutions of 5-20 mM NaCl and HCl in DI water were tested, corresponding to conductivities of 0.48-2.3 mS/cm and 0.77-5.2 mS/cm for NaCl and HCl, respectively. Sprays were generated with a constant 18 V_{amp} AC input voltage.

As expected, the output current increased monotonically with solution conductivity as shown in Figure 4.10(a). When the limiting molar conductivity is accounted for, by multiplying with the solution concentration, all the data is plotted on a logarithmic scale and all the data for the most part collapse, as shown Figure 4.10(b). A value of n = 0.35 can be extracted from a linear curve fit, consistent with the expectations according to Eq. (4.2). Curve fits of the individual solution data yield values of n = 0.45 and 0.37 for NaCl and HCl, respectively, which are also consistent with Eq. (4.2).

Figure 4.10: (a) Logarithmic plot of output spray current for different (a) concentrations and (b) conductivity of HCl and NaCl in DI water with an applied voltage of 18 V_{amp}. The dash line in (b) is a linear curve fit with a coefficient of determination equal to r^2 =0.76.
4.2.7 Analysis of the Load Resistance and the Input Current

One notable by-product of increasing the solution conductivity is that the input current to the PT also increased. The input current applied to the PT was measured using an oscilloscope (Tektronix DPO 2024B) for spray of HCl and NaCl solutions, each using an 18 V\textsubscript{amp} input voltage. Figure 4.1 shows the input current as a function of the solution concentration, so that, the input current increases monotonically with solution concentration and thus conductivity. The author attributed this to the fact that increasing the conductivity effectively decreases the output load resistance.

![Graph showing input current as a function of concentration](image)

*Figure 4.11: Input current for different concentrations of HCl and NaCl in DI water for an input voltage of 18 V\textsubscript{amp} and slightly different frequency around 60 KHz dependent on the liquid.*

The author simulated equivalent circuit for the piezoelectric transformer\textsuperscript{15} using LT Spice software (Figure 4.12(a)), and the effect of the change in the load resistance was investigated. Results showed that for smaller values of load resistance, both the input and output current of the piezoelectric transformer were increased, as shown in Figure 4.12(b). According to these results, decreasing the output load resistance increases the input current and total power consumed by the PT, which is consistent with increasing the conductivity of the solution (reducing the load resistance) as discussed before.
4.2.6 Effect of Liquid Conductivity and Surface Tension on the Onset Voltage

The increase in the input current (and thus power) with conductivity for a fixed input voltage of 18 Vamp potentially suggested that the minimum input voltage to onset the spray, \( V_{in,\text{onset}} \), is also a strong function of the conductivity. The onset voltage is set by the Maxwell pressure induced by the electric field at the end of the PT, which must overcome the surface tension, \( \gamma \), of the liquid film to induce a spray. If it is assumed that the output voltage at the edge of the PT is linearly proportional to the input voltage \( V_{in} \), as suggested by the measurements of the output voltage, it is anticipated that

\[
V_{in,\text{onset}} \propto \gamma^{0.5} (\lambda_m C)^{-0.5}
\]  

(4.3)
Figure 4.13(a) confirms that the onset voltage does decrease non-linearly with ionic concentration. It is important to note that, for all of these studies, the surface tension was measured to be 73 dyn/cm, when the conductivity was varied, which precludes the possibility that surface tension was causing the variations in current and voltage that were measured. The surface tension of solutions was measured using an FTA 100 Angstroms instrument. A 4 mL syringe was used to inject the solution through the device, and results were obtained by calculating the average of three different sequential measurements.

Interestingly, the exponent factor was measured to be -0.32, which is slightly lower than the expected relationship from a simplified balance of Maxwell pressure and surface tension or electrostatic and capillary pressure\(^{17}\). While this could be attributed to the effect of mechanical vibration on the atomization, further study is required to resolve this completely. Nevertheless, the general trend is consistent with the argument that the electric field induced by the PT is primarily responsible for inducing the spray.

![Figure 4.13](image)

**Figure 4.13:** a) Logarithmic plot of the onset voltage for various concentration of NaCl in DI water. The dash line is the linear curve fit with a slope equal to -0.32. b) Onset voltage as a function of surface tension for various concentration of glycerol in DI water.

To explore the effect of surface tension, the polar solvent glycerol was added to aqueous solutions of NaCl (0.53 mS/m) to reduce the surface tension from \(\gamma = 73\) to 69 dyn/cm (corresponding to glycerol concentrations from 0.01-200 mM). As expected, the onset voltage
increases as $\gamma$ increases (Figure 4.13(b)). However, unexpectedly, both the spray output current and PT input current were unaffected as the surface tension was varied for a constant input voltage. For the same input voltage ($21 \text{ V}_{\text{amp}}$), the input current ($i_{\text{rms}}$) for all the samples was essentially 84 mA, and the spray current ($i_{\text{spray}}$) was 20 nA. As the surface tension does not impact the output load resistance, it is not surprising that the PT input current was not affected. But Eq. (4.2) shows that the spray current should be proportional to a positive power of the surface tension. The author attributed this anomaly to the fact that the resolution to detect the expected minute changes in current (~0.0001%) was not sufficient as predicted by Eq. (4.2) for the small range of surface tension values explored here. But it is possible that there may be more than conventional electrospray mechanisms at play, altering the dependence of these parameters on surface tension.

4.2.7 Chemical Solution Preparation

Sodium chloride (NaCl), glycerol and Hydrochloric acid (HCl) were purchased from Sigma Aldrich. Aqueous solutions at different concentrations were made by diluting using deionized (DI) water (18 MΩ). Solutions of 5-20 mM NaCl and HCl in DI water were prepared, which corresponds to conductivities of 0.48-2.3 mS/cm and 0.77-5.2 mS/cm for NaCl and HCl, respectively.

4.4 Summary

This chapter provided a novel approach to create a spray generation system using a piezoelectric device. A detailed report of this work including the piezoelectric transformer and stand design, spray generation, spray coating profilometry, volumetric flow estimation, linear flow speed visualization, bulk motion of the droplet directly on a PT device, measurement of output voltage, effect of solution conductivity on the output current, analysis of the load
resistance and the input current, effect of liquid conductivity and surface tension on the onset voltage and chemical solution preparation has been presented.

To summarize, the author successfully generated a continuous spray by pinning a 128°YX LiNbO₃ piezoelectric crystal in the standing wave mode and providing the desired liquid film using a paper wick. The paper covers the PT width which enabled a final spray that was as wide as the PT device. Profilometry of the coated area by the generated spray demonstrated a uniform coating. Volumetric flow rate of the produced spray was measured to be 12-30 µL/min, depending on the exact experimental conditions (input voltage, spray solution) and the front dye tracking proved the pumping effect of the PT device. To verify whether electrical or mechanical feature of the piezo electric crystal is the dominant reason for the spray generation, bulk motion of the droplet was recorded.

The output voltage gain of the PT was measured to be 124 and compared to the calculated value. Different concentrations of HCl and NaCl in DI water were used for spray generation and results showed that the liquid conductivity and the spray current are monolithically related as it is predicted in a conventional electrospray system. The simulations done by the author also indicated that the input and output current increased when the liquid conductivity was elevated. The minimum voltage for liquid film breakage was shown to decrease as the liquid surface tension reduced.

4.5 References


5.1 Introduction

Layer-by-layer (LbL) deposition of multilayer films has been widely used in the fabrication of various sensors including gas, humidity, and bio sensors\(^1\). The LbL deposition method entails alternating deposition of oppositely charged ions to form stable multilayer films via electrostatic interactions or hydrogen bonding\(^2\). There are many approaches of building multilayer films such as dip coating\(^3\), inkjet printing\(^4\), spin-assisted assembly and electrophoretic deposition\(^5\). However, scalability and thin-film uniformity are still challenging for commercialization of these techniques.

5.1.1 Spray Coating Techniques

Spray technologies have been investigated for their potential capabilities of material coating. There are various methods of breaking the liquid droplet down to the spray. One of the simplest and widely used approach is a pneumatic spray which does not contain a precise or uniform droplet size and hence is not a proper choice for use in membrane coating. Among the vibrational approach of spray generation, surface acoustic wave atomizers have been utilized for material coating. Although this technique provides a uniform coating, the complicated procedure to fabricate this device along with the 100 V range of required input voltage can undermine their efficiency\(^6\).
Electrosprays are well known to form a reliable continuous spray from a liquid sample. However, the need of high input voltages (kV), along with costly equipment, does not make it an apt choice in large scale sensor fabrication processes. Moreover, the principal of the electrospray phenomenon is based on the Taylor cone formation and droplet plumes produce a circular injected area which is not ideal for uniform material coating.

5.1.2. Membrane Coating Materials

Among the other coating methods, polymer coating techniques have been witnessing a rising demand due to the vast range of applications for polymer coated membranes in fuel cells, solar cells, isopropanol dehydration, surface treatment of metallic coronary stents and the next generation of drug delivery systems.

The key factor in membrane coating is to find a balance between flux and separation. In other words, the liquid flow rate through the membrane needs to stay significant, while the target ions are blocked by the coated membrane. It has been proved that alternating coating of a membrane with opposite charge polymers can produce a thin film. Layer by layer deposition of anionic and cationic polyelectrolytes such as poly (allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS) on a solid membrane was shown to be successful in the separation of ethanol and water mixtures.

Ouyang et al. reported that adding a layer of poly(diallyl-dimethylammonium chloride) (PDADMAC) to the ion rejection membrane, coated with other polymers, enhances the liquid flux through the membrane by increasing the swelling of films contacting the PDADMAC.

Here, the author demonstrated an innovative procedure for LbL thin film deposition using a piezoelectric driven spray generator. As a proof-of-concept, some of the previously
used polymers for membrane coating such as poly (allylamine hydrochloride) (PAH), poly(styrenesulfonate) (PSS), poly(diallyl-dimethylammonium chloride) and poly(diallyl-dimethylammonium chloride) (PDADMAC) were sprayed using the novel PT-driven spray formation technology introduced by the author in chapter 4. A polycarbonate track-etched (PCTE) membrane was spray coated by the polymer mixtures and water permeability and ion rejection ratio of the final PT spray coated membrane were measured. As a proper solvent for polymer based mixtures, dimethyl sulfoxide (DMSO) has been widely used due to its nontoxicity, polymeric and water solubility capabilities, hence the author included this chemical to the spray formation list to examine the ability of PT spray formation technology for different probable polymer mixtures. This method has several advantages due to its cost efficiency, quick response and low material consumption when compared with the traditional thin film deposition methods.

5.2 Experimental

5.2.1 Spray Generation Setup

Spray formation was achieved via the same PT driven setup mentioned in previous chapter. A 15 mm (or 30 mm) × 100 mm × 1.5 mm (w/l/t) 128°YX lithium niobate (LiNbO₃) crystal was purchased, and bottom and top electrodes were painted on the PT surface using silver paint (conductive silver paint from SPI company). A PT stand was designed and fabricated using a 3D printer to mount and pin the PT at two locations corresponding to nodes in the displacement wave related to second resonant frequency, which was around 60 KHz and 63 KHz for 15 mm and 30 mm width PT devices, respectively. A signal generator and a radio frequency amplifier provide the required input current at the desired frequency. A liquid sample
was delivered to the surface of the PT by a paper wick placed between a liquid reservoir for coating material and the PT surface.

5.2.2 Material Preparation

PAH (15 kDa), PSS (70 kDa) and Poly(diallyldimethylammonium chloride) (PDADMAC) (20 wt. % in H₂O) in liquid form were purchased from Sigma-Aldrich. Aqueous solutions of the polyelectrolytes at 20 mM (based on repeat unit molecular weight) were prepared. The pH of the PAH and PSS solution were unadjusted. A PCTE membrane (pore diameter: 50 nm, membrane thickness: 10 μm, porosity: 3×10⁸ pores/cm², Whatman) was used as a template.

5.2.3 Moving Stage (Lazy Susan)

To provide a moving stage for high throughput membrane coating, a circular, slow spinning stage (lazy susan) was designed and made by the author (Figure 5.1).

A DC gear box reduction motor was used to produce 5 RPM vertical spinning motion by applying 12 V input voltage delivered by a DC power supply. To change the motion to a horizontal direction, a vertical shaft worm gear box was connected to the motor. This shaft also reduced the speed of spinning 30 times due to the size difference. A gearbox ratio of 30:1 means that the output side is about 30 times faster than the input side. This gear box works using a 30:1 ratio worm drive, which is able to hold the position when the power is not applied to prevent any interference in the experiment result when any electrical interruptions occurs.

A 10 inch diameter plexiglass sheet was used as the moving stage connected to the motor shaft. A simple variable power supply driver motor was also used to change the power delivered to the motor by a resistor based voltage divider. The author used this configuration
to control the motor speed, which leads to the variable plexiglass speed of spinning. This enabled the exposure of the membrane with the coating spray for different time durations. The whole structure was mounted on an aluminum sheet for support and stability.

![Figure 5.1: Sequential PT driven Spray coating of membrane using PAH and PSS by placing the membranes on a Lazy Susan.](image)

### 5.2.4 Water Permeability and Salt Rejection Tests

The PT-driven spray coated membrane was placed in a water filled cell (Amicon model 8003) and stirred. A pressure of 4 bar was applied to drive water through the membrane, which was collected in a small beaker. The collected mass was measured using a scale, which was connected to a PC with a LabVIEW™ based program for data acquisition and recording the change in mass over time. The hydraulic permeability of the membrane was calculated using the slope of this graph.

In salt rejection tests, 10 mM solutions of single salts (i.e., KCl, MgCl₂) were used as the feed solutions and a pressure of 4 bar was applied to drive the flow. The solution was collected in a glass reservoir. Ion chromatography (Dionex ICS-5000) was used to analyze the
concentration of ions in the feed ($c_f$) and permeate ($c_p$) solutions. The percent rejection, $R$, was calculated according to

$$R(\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100$$

(5.1)

5.3. Results

5.3.1. Bilayer coating of PAH and PSS

A paper was placed between a reservoir which contained PAH or PSS solution and PT surface. Autor found it useful to soak the paper in the reservoir in the beginning of the experiment to provide a better contact between the paper and the PT edge which can enhance the uniformity of the generated spray. The PCTE template membrane was placed 3 cm beneath the PT on the moving stage. By introducing around 15 V\text{amp} AC input voltage in 59.8 KHz frequency, the spray was generated. The spray was formed along the width of the PT, which is 15 mm in this experiment, and the spray droplets are of sufficient size that fall to the surface beneath in the PT (in a manner analogous to a shower). As such, the spray deposits over an area of 15 mm by 0.5 mm. Membrane was exposed to PAH spray for 30 seconds and after drying up, which took almost 5 minutes, PSS was sprayed over the membrane for 30 second to from the first bilayer coating of the membrane.

The process was repeated to form multiple bilayers and to coat the PCTE membrane completely. Repeated spray coating of the membrane using PAH and then PSS resulted in the fabrication of multilayer thin films on the membrane surface. As shown in Figure 5.2, scanning electron microscope (SEM) images revealed that the native 50 nm diameter pores of the bare PCTE membrane were coated by the sprayed polymers until total coverage was achieved.
Figure 5.2: SEM images of PCTE membranes sprayed with different numbers of bilayers. Different numbers of PAH/PSS bilayers were sprayed onto a 50 nm PCTE membrane. The sprayed membranes were taped onto a SEM grid, sputtered with iridium (2 nm), and visualized in SEM.

Table 5.1 shows the results for water permeability performed for bare, 1 bilayer, 2 bilayers, and 3 bilayers coated membranes using 30 s spray durations for each layer. The water permeability decreased rapidly with increasing number of bilayers, suggesting that a successful LbL thin film was sprayed on the PCTE membrane. The sprayed LbL thin film also showed higher salt rejection at a higher number of sprayed bilayers. The water permeability of the membrane sprayed with three bilayers was not measurable, indicating the pores of the membrane were completely blocked by the sprayed films.
Table 5.1: Water permeability and ion rejection results for PAH/PSS PT \textsubscript{spray} coating.

<table>
<thead>
<tr>
<th>Number of bilayer</th>
<th>Water permeability L/m\textsuperscript{2}/hours/bar</th>
<th>Ion rejection ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 bilayer</td>
<td>41±5</td>
<td></td>
</tr>
<tr>
<td>2 bilayers</td>
<td>3.5</td>
<td>25% for 10 mM NaCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32% for 10 mM MgCl\textsubscript{2}</td>
</tr>
<tr>
<td>3 bilayers</td>
<td>Too slow</td>
<td></td>
</tr>
</tbody>
</table>

In some cases, it is desirable to prepare thin films with a high number of bilayers while maintaining membrane permeability. This condition can be achieved by shortening the PT spray durations. A duration of 10 s was used instead of 30 s to alternatingly spray PAH/PSS bilayers. Figure 5.3 shows a logarithmic plot of how the water permeability changes with different number of bilayers. The water permeability decreased from 425 L m\textsuperscript{-2} hr\textsuperscript{-1} bar\textsuperscript{-1} for the bare PCTE membrane to 0.9 L m\textsuperscript{-2} hr\textsuperscript{-1} bar\textsuperscript{-1} with 5 bilayers. The water permeability was unmeasurable for the membrane with 6 bilayers. The results show that by shortening the spraying duration, a thinner film is deposited for each bilayer. The small values of the water permeability of the coated membrane suggest the absence of big defects in the LbL films.
Figure 5.3: Logarithmic plot of the normalized water permeability vs. number of bilayers. A 50 nm PCTE membrane was used as the substrate membrane with a different number of sprayed PAH/PSS bilayers with 10 s durations. The water permeability test was measured in a dead-end filter cell. The error bars meant three measurements with the same membrane and were barely seen since they were smaller than the symbols.

Figure 5.4: Salt rejection vs. number of bilayers. A different number of PAH/PSS bilayers were sprayed alternatingly with 10 s duration on a 50 nm PCTE membrane. The salt rejection test was carried out in a dead-end filter cell filled with either 10 mM KCl or 10 mM MgCl₂.

Figure 5.4 shows how the rejection of 10 mM KCl and MgCl₂ changes with the number of bilayers sprayed on the PCTE membrane. The results illustrate that by increasing the number of bilayers, a higher salt rejection is achieved for the sprayed membrane.

Since there is no waste of coating material, unlike dip coating approach, the amount of the required polymer solutions for membrane coating is considerably decreasing. The membrane diameter is 2.5 cm while the moving stage diameter is 25 cm, which makes it possible to mount 30 membranes on the moving stage simultaneously. If the speed of spinning
in moving stage is set to expose each membrane with the PT spray for 20 second, bilayer coating of 30 membranes is possible within 26 minutes. This can prove the capability of this PT driven spray generation approach as a high throughput membrane coating system.
5.3.2. PDADMAC Spray Coating

To prove the ability of this novel spray formation technology for polymer coating of the membrane, PDADMAC was tried.

The membrane was placed on the Lazy susan, at a distance of 3 cm below the PT device. A DC motor was reconfigured to provide a 0.1 cm/s spinning speed for moving the stage. The author exposed the membrane with PT driven spray of PDADMAC for 25 s. A mixture of 0.1 Molar of PDADMAC and 1% poly vinyl alcohol (PVA) was diluted 33% with DI water to provide the coating material for the membrane. Table 5.2 shows the results for this experiment.

<table>
<thead>
<tr>
<th>Number of layer</th>
<th>Water permeability</th>
<th>Ion rejection ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 layer</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>3 layers</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>6 layers</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>20 layers</td>
<td>50</td>
<td>66% ± 2 for 10 mM KCl</td>
</tr>
</tbody>
</table>

The results represent the capability of the system for spray production. Applying just 12 Vamp to PT was sufficient to generate a uniform continues spray from the PDADMAC solution. The water permeability was almost as high as a bare membrane with no coating layer in the first 5 layers coating. The author attributed this to the dilution factor used for the coating mixture. The results suggest that the percentage of the polymer per sprayed droplet was very low in the first stages of the coating.
5.4 Summary

A piezoelectric transformer was used to generate a uniform spray by applying 15 to 25 V_{amp} to the crystal at its second resonant frequency. A continuous supply of solution from a paper wick was delivered to the surface of the PT, without the need for an external pump. Layer-by-layer spraying of multilayer thin films with PAH/PSS and PDADMAC were used as a model system to demonstrate the PT-driven spray technique as a material-deposition method. Results show that the spray duration and number of bilayers have a significant impact on the water permeability and salt rejection of the sprayed membrane.

5.5 References


CHAPTER VI
CONCLUSION

6.1 Conclusion

In this dissertation, the author has successfully developed a piezoelectric based system for fluid manipulation. Piezoelectric devices produce mechanical strain under applied electrical field, which results in propagating mechanical vibration. This acoustic wave has been used to manipulate the liquid medium in sensing technologies due to their benefits such as small volume of required sample, high sensitivity, bio-compatibility and non-invasive procedures. The high sensitivity arises from the large electromechanical coupling factor of the piezoelectric crystal.

Moreover, the aforementioned features make piezoelectric devices also apt choices in actuating systems such as spray formation. The mechanical vibration along with the large polarization produced on the surface of the piezoelectric crystal can be used to overcome the liquid film surface tension and break it into the droplets.

In this work, a piezoelectric based sensor, which employs photolithographically patterned electrodes was used for sensing applications. In addition, the author explored the possibility of using piezoelectric transformers to generate a continuous uniform spray by applying low input voltages when compared to the conventional spray production techniques.

The dissertation was organized and pursued in three projects in order to achieve the research outcomes.
In the first project, an efficient piezoelectric based detection sensing system for the detection of heavy metal compounds was developed. A photolithographically fabricated piezoelectric sensor, which incorporates Au IDEs was used for the detection of various heavy metal compounds. Proper sensitive layers were chosen for the selective detection of the heavy metal compounds including lead, cadmium, nickel and mercury nitrate. Based on the results from the piezoelectric sensor, the author concluded the capability of the developed piezoelectric based system to detect heavy metal compounds at pico molar concentration levels using the frequency shift.

The author was responsible for design and fabrication of the SAW device and finding proper sensing layer. Experiment setup and controlling the environmental factors in order to preserve the experiment repeatability was also done by author.

In the second project, the author designed and fabricated a novel piezoelectric transformer for fluid manipulation and spray generation. A micro fiber glass paper was used to wick the liquid film out of the contained reservoir. Based on the imaging results, a large area uniform spray was generated along the width of the piezoelectric transformer. The author demonstrated that bringing a thin-film of liquid to the surface of a PT via a wick generated a spray of droplets. The author’s studies strongly suggest that the spray mechanism is electrospray in nature, and thus parameters such as solution conductivity and surface tension can be used to manipulate the spray behavior. By spraying directly from the wick/PT interface, the nebulization in many ways resembles a free-surface electrospray rather than capillary electrospray. In the author’s opinion, the broad area nature of the spray makes it very appealing for emerging applications in materials synthesis and coating, were uniform deposition may be possible over large substrates simply by scaling the size of the PT crystal.
The author was responsible for design and fabrication of the device and stand. Proper experiments were designed and conducted by author to study the key factors of this phenomenon.

In the third project, the author tried to use the PT spray generation system for coating purposes. Some previously proven polymeric materials for membrane coating were chosen: poly(allylamine hydrochloride) (PAH), poly(styrene sulfonate) (PSS) and (PDADMAC) were sprayed on to a polycarbonate track-etched (PCTE) membrane. SEM results illustrated the polymer thin film formation on the membrane. Water permeability and ion rejection ratio of the coated membrane were measured. The author concluded that the number of layers has an optimum number for each desired polymer coating material and it occurs where the polymer film is uniformly coated on the membrane surface to result in a good ion rejection ratio, while the polymer film is still not too thick to block the liquid flow through the coated membrane.

There are several possibilities to improve the current projects which are covered in this dissertation. The author has some suggestions for further studies:

- The ability to integrate the SH-SAW sensor into a hand-held and portable detection system.
- Improve the selectivity of the SH-SAW sensor to exposed chemicals by studying target to sensing layer binding conditions.
- Enhance the experiment repeatability by exploring the other methods of the sensing layer deposition which results in a uniform film.
- The effect of the piezoelectric transformer geometry on the discharge points of the edge of the PT device can be investigated using software simulations such as COMSOL.
- The resultant aerosols size and dispersity can be measured using video graphic techniques.
• More suitable approach of liquid delivery to the PT surface needs to be found to increase the produced spray uniformity along the width of the PT.

• The dependency of the spray formation towards the liquid conductivity and surface tension can be the focus of the further studies to investigate the capability of the system for spray generation from the nonconductive solutions.

• The influence of the spray duration, temperature and PT to membrane distance on the ion rejection ration can be investigated to find the optimized condition.

• Since the positive affect of washing the membrane proven in the conventional LBL membrane coating on the membrane function has already been proven, a washing step can be added in between the two spray stations above the moving stage.

• PT-driven spray technique can be extended to the layer-by-layer deposition of a large variety of polymer materials for the rapid, scalable synthesis of ion-exchange and ion-rejection membrane sensors.
Appendix A
List of publications

A.1 Inventions

A.1.1 Intellectual Property


A.1.2 Patent


A.2 Journal Papers


A.3 Conference Papers


Appendix B

Matlab code for scale used to graph the spray volumetric flow rate used in Chapter 4

```
function curpre

obj1(1)=serial('COM5','baudrate',2400,'databits',7,'parity','none','flowcontrol','none','terminator','CR/LF');  %from balance user manual

for i = 1:length(obj1)
    fopen(obj1(i));
    fprintf(obj1(1),'P');
    fscanf(obj1(1));
end

t1=timer;
t1.startdelay=1;
t1.startfcn = @starttimer;
t1.TimerFcn = {@collectdata,obj1};
t1.StopFcn = {@stopdata,obj1};

%--------------------------------------
t1.Period = 0.1;       %time between readings in seconds

%--------------------------------------
t1.TasksToExecute = 4000;  %number of readings

%--------------------------------------
t1.ExecutionMode = 'fixedSpacing';
```
start(t1)

function starttimer(t1,event)

 t0=event.Data.time;

 data=[0 0];

 assignin('base','data',data);

 assignin('base','t0',t0);

 function collectdata(t1,event,obj1)

 fprintf(obj1(1),'P')


 ot=fscanf(obj1(1))

 out=sscanf(ot,'%f %*s');

 tn_ = event.Data.time;

 t0_=evalin('base','t0');

 assignin('base','data',vertcat(evalin('base','data'),[etime(tn_,t0_) out]))

 function stopdata(t1,event,obj1)

 for i=1:length(obj1);

 fclose(obj1(i));

 delete(obj1(i))

 clear obj1(i)

 end

 delete(t1)

 clear t1

 display('Timer ended');