ABSTRACT

**INKJET PRINTING POLYMERIZED
PCDA AS A MEANS OF SERIALIZATION**

By
Constantino Stavrou

Polymerized PCDA, otherwise known as pentacosadiynoic acid, due to its color changing response to high temperatures, has been used as a means of indicating whether the material has been exposed to high temperatures. Quick-Response codes or Q-R codes have been used as means of serialization due to their two-dimensional design, allowing for the embedding of larger amounts of information than their one-dimensional barcode predecessors.

Combining the colorimetric response of PCDA polymer with the information coding powers of Q-R codes, an improved version of the Q-R Code is made, which was used not only for serialization purposes, but as a means to provide visual indicators as to the temperature the item is exposed to. This can be used to quantize the quality of the product in question. These results are read out by an application which is adapted to an Apple smart phone.

Usage of purified PCDA in a chloroform solution shows to provide clearly printed Q-R codes which could be read by the application, which proves that the difference in color does not affect the capability of the code to be read. A comparison of the reflection of each color to the white paper background shows that the range of temperatures where the codes changes color is very large, spanning from 20% light reflected to 60% light reflected for the color red, 20% light reflected to 40% light reflected for green and 40% light reflected to 50% light reflected for blue. There is no obvious ratio of red, green, and

blue that could be used in order to find a usable function of temperature versus color without use of more advanced analysis algorithms. The PCDA exhibits the onset of color changes around 50 to 55 degrees Celsius, while having a vigorous color change around 65 degrees Celsius, and finally reaches its maximum color change at 75 degrees Celsius for the water based ink. The PCDA shows color change for the chloroform-based ink at 65 degrees Celsius and steadily increases in the color red until around 85 degrees Celsius when a maximum is reached. The reflectivity spread for the chloroform-based ink is slightly less than the water-based, ranging for red ranging from 40%-70%. However, it gains spread in the blue and green ranging from 60%-90% and 45%-70%, respectively. The use of chloroform leads to the degradation of the inkjet nozzle head however, and careful selection of printing heads that does not degrade with the intended solvent should be exercised. While the water-based solution is shown to work, it requires many more layers to be printed to make the design as dark as the chloroform-based, as well as having a lighter shade of blue than the chloroform-based after UV treatment, which makes it unable to be read by the application, which is calibrated for the chloroform based ink.

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CHAPTER 1

INTRODUCTION

1.1 Objective

The objective of this dissertation is to incorporate visual indicators into Quick Response (Q-R) codes to provide dynamic sensory information in addition to the alpha numeric coding which is embedded. Using PCDA, or pentacosadiynoic acid, one can use a section of the Q-R code to print an ink whose color changes with temperature thereby enabling temperature sensing by the Q-R code. Since Q-R code retrieval algorithms are based on the shapes of the code elements rather than their color, an entire Q-R code does not have to be one material or color in order to be read, leaving the possibility for multiple types of color changing inks that respond to other stimuli, such as mechanical strain, presence of chemical stimuli, etc, providing even more sensory indicators into the code. In short, the Q-R code was fabricated using an inkjet printer, such that the top left square which encompasses a fourth of the code was printed with an ink fabricated with PCDA while the rest of the code is printed with regular black ink. This Q-R code is heated to induce the color-change and the phone application is used to record the color change, as well as read out the message embedded into the Q-R code. The phone app incorporates open source code for reading the Q-R code alphanumeric message. In addition, the phone app analyzes the RGB color in the top left quadrant of the Q-R code to interpret the color of the PCDA ink and the temperature to which the code has been exposed. In the next section, background information on key technical components, which significantly contribute to the development of the sensory Q-R code, are presented. Data acquisition can be seen illustrated in Figure 1.1
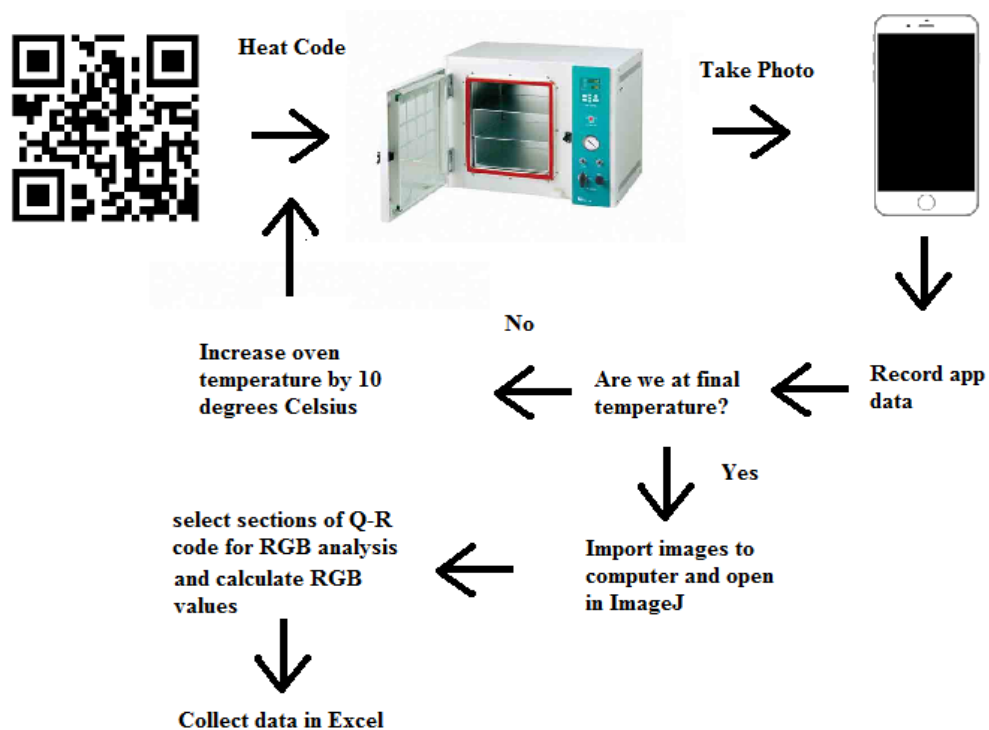
Figure 1.1 Flowchart of the process of acquiring and processing the data.

1.2 Background Information

1.2.1 Polydiacetylenes

As described in a recent NJIT PhD thesis, Polydiacetylenes are invaluable for their ability to alter their chromatic properties when acted upon by one of several outside stimuli. Being able to change colors when exposed to high temperatures, inducing the polymer lattice with mechanical stress, or even exposing the polymer to certain chemicals, is a property that is unique to PDAs. When the PDA monomer is polymerized through exposure to radiation, ranging from UV to γ-rays, it turns blue. This signals that the absorption in the red spectral region has become stronger as the electrons move from the π to the π* absorption band. [1]

Polymerization
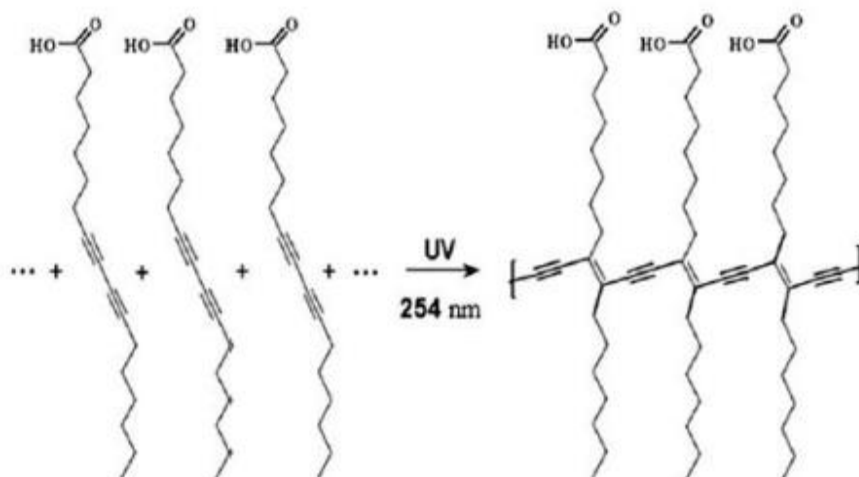
Figure 1.2 A model of PDAs molecules when exposed to UV radiation.
Source : [2]

After polymerization, the π electron conjugation length increases. This increase in length is caused by the hydrogen bonds creating a strain that is put on the head group. This strain on the head group is easily disrupted which will release the strain that is holding the side group. This disruption can come in the form of heating as well as many other stimuli. Once this strain on the head group is released, the backbone structure of the PDA will deform and twist, decreasing the conjugation length and changing the color of the PDA and decreasing its strong absorption in red. Visually this is shown as a change in colors of the PDA, from blue to red. [1,2] A visual interpretation of this can be seen in Figure 1.3.

Beyond its chromatic properties, PCDA has been widely studied because it is very versatile and can be physically altered to many useful configurations. PDAs have been made into vesicles, where the PDA would encase a molecule, creating a protective shell

around the molecule. PDAs have also been organized into Langmuir mono-layers, self-assembling films, and even single crystal configurations. Along with PDA configurations that just use PDA, they have also been incorporated into other matrices. The PDA is introduced into inorganic configurations, other polymers, and even living cells, while still maintaining its chromatic property. This makes PDA ideal for being used inside systems where visual indicators are necessary.

In the world of biosensing, most applications that use PDA require that the head groups be chemically modified so that biomolecular recognition units and other functional components are implemented at the surface of the PDA structure.
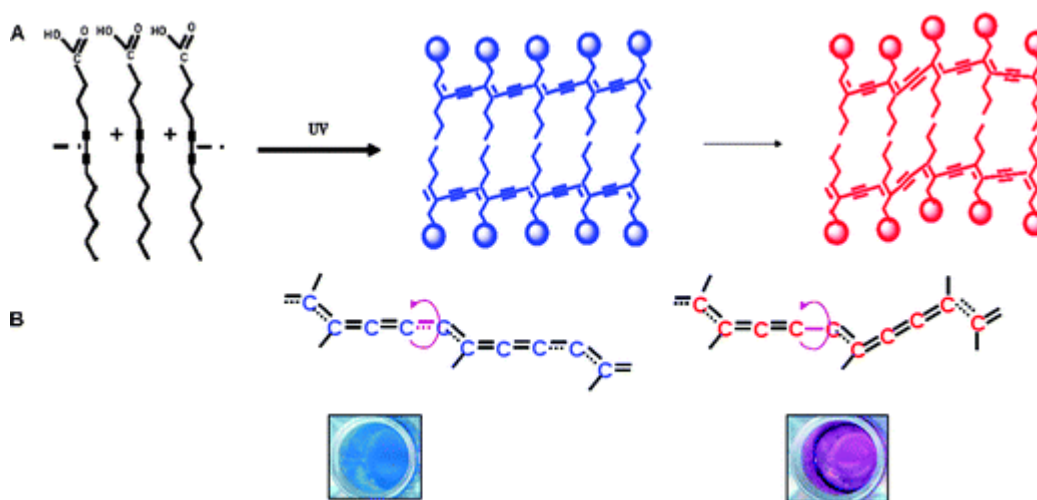
Figure 1.3 A model of PDAs before UV treating, after UV treating, and after stress has been given to the head groups.
Source : [3]

One such example would be the implanting of Biotin in the PDA vesicular frame work in order to detect interactions between the Biotin and Streptavidin. The high affinity between soluble streptavidin and the PDA–biotin complex gives rise to the blue–red transition, accompanied by vesicle aggregation due to the multimeric interactions involving streptavidin and four biotin units. Figure 1.3 demonstrates this streptavidin-biotin reaction using the fluorescence from PDA vesicles at 543 nm at different

concentrations of streptavidin. The red phase of the PDA vesicles can be seen more vividly when the concentration is larger and it becomes less prominent as the concentration is decreased. [4]
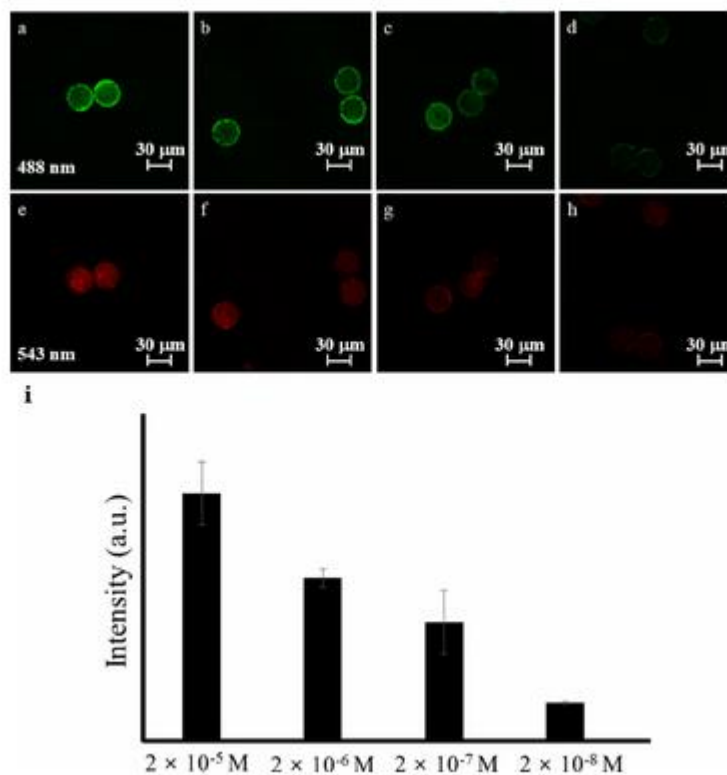
Figure 1.4 CLSM images showing biotin-streptavidin interaction by measuring the fluorescence of FITC on streptavidin at 488 nm (a – d) and the fluorescence of PDA at 543 nm (e – h). The concentrations of streptavidin were (a, e) 2 Â 10 À 5 M (100 m L), (b, f) 2 Â 10 À 6 M (100 m L), (c, g) 2 Â 10 À 7 M (100 m L), and (d, h) 2 Â 10 À 8 M (100 m L).
Source : [4]

Past experiments using the PDA structure have proven that the versatility of PDA, allows for vastly different methods for colorimetric detection of proteins, nucleic acids, and whole microorganisms. This was done by incorporating the specific receptor into the PDA vesicle framework. One such example can be seen in one research paper, where sialic acid residues were attached to the surface of the PDA vesicles, which were used in the detection of influenza virus. PDA-Lipid systems were one of the earliest

systems to make use of the PDAs chromatic features and stable structure. Using their reaction to cholera toxins, gangliosides were introduced into the PDA vesicle framework, creating a sensor for viral detection. These, among many other examples demonstrate the sturdiness of the PDA structure and the versatility of PDA vesicles.[5,6]

PDAs were first discovered in 1969 by German scientist Gerhard Wegner during his work with 1,6-bishydroxy hexa-2,4-diacetylene. Shining UV light on his sample he created the first PDA. He suspected that this polymerization was due to a mechanism in which the bonding between subsequent PDA molecules creates a conjugated backbone in the structure which is held together with 3 double bonds which repeat in a pattern throughout the structure. Although this was supported by the polymers optical and mechanical properties as well as the evidence shown by x-ray and electron diffraction studies, they were not confirmed until 3 years later when American scientist Raymond H. Baughman found the spatial requirements for these PDAs to polymerize.[7,8]

Raymond H. Baughman used X-ray diffraction to measure the necessary structure change for polymerization, finding the spacing between monomer molecules inside 2,4 hexadiynediol to be .044nm and the rotation of what he calls the "molecular rods" is about 28 degrees, which suggests that because there is so much energy needed for rotation, that this energy contributes significantly to the energy needed for polymerization to occur. [9]

1.2.2 Q-R Codes

Q-R codes, or quick response codes, have been experiencing a large increase in popularity in commercial usage. Universal Product Code (UPC) barcodes have been the standard way of serializing products in stores to label product. The UPC barcode however lacks the power in storage capacity of the Q-R code. Its two-dimensional design allows for much more data storage than the UPC barcodes. Solid blocks in the design are utilized for several purposes in the Q-R Code. [10,11] As shown in Figure 5, it contains 3 square sections highlighted in purple, labeled Positioning, located at the top left and right corner as well as the bottom left corner of the design. The region in red indicates what type of format the code is using by the reading of the blocks or lack of blocks immediately on the outside of the large square sections. The sections of the code that are boxed off in blue are where the version information is coded. One or several smaller square parts which are highlighted in green, labeled Alignment, are put through the code periodically to ensure that the Q-R code reader is processing the image in the correct orientation. The amount of alignment squares depends on the amount of information that is being coded. The areas that are not highlighted are the data inputs as well as data points to help during the error correction process. The appearance of blocks or lack of appearance of blocks provides a horizontal and vertical component for writing messages.
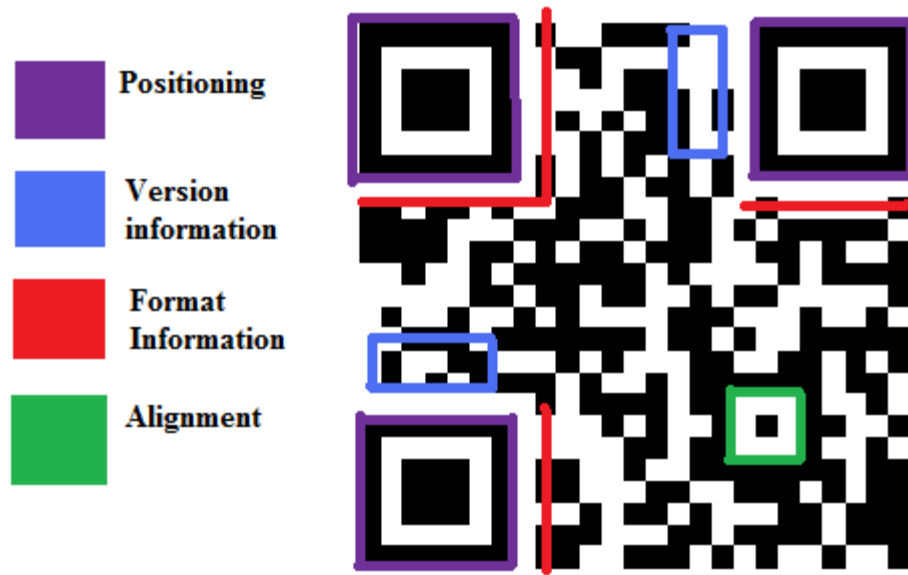
Figure 1.5 Model of the Structure of a Q-R Code. The encoding of information in the structure is described in the text above.

The design is corrected for errors using the Solomon-Reed error correction algorithm. There are different levels of this type of error correction which all vary in terms of the amount of errors that can be corrected and the amount of data that can be stored. The more data errors that can be corrected by the application reading the code, the less storage capacity the designs possess.[10,11]

QR Codes were created by a Japanese car parts company called Denso Wave in 1994. Originally the QR codes were used for tracking parts for vehicle manufacturing. Because of its capacity to encode more data than the normal bar-code, it soon spread as a means of commercial advertisement which paired with the sales of smart phones a few years later. This provided a means of the average person to be able to read these bar-codes through the convenience of a phone app and boosted the marketing industry. [11]

1.2.3 Inkjet Printing

Inkjet printing has become a staple in the office world, with its ability to print words, pictures, etc onto paper. This technology is seeing some very interesting applications in research as of recently, however. With printers that are capable of printing various types of inks, and even materials that are solid at room temperature, it has proven to be a valuable tool in engineering. Inkjet printing was developed in the 1950s by Epson, Hewlett-Packard, and Canon. Within the next 20 years, inkjet printers would be able to connect to a computer and using special software, recreate digital images. They would hit the market and skyrocket in popularity for both personal and professional use. There are two different types of inkjet printers, drop on demand or DoD and continuous inkjet or CIJ.

Although the idea of the CIJ was actually developed in the 1867 with the invention of the siphon recorder, a device that would turn a telegraph message into a wavey line that would be interpreted by a trained telegrapher, the idea was put to a more practical use in 1951 by the company Siemens with their development of a medical strip chart recorder. The idea of the CIJ is that the inkjet head is constantly dropping ink and the ink is directed using 1 of 2 different methods. Piezoelectric crystals in the case of the Siemens chart recorder are the method used to this day due to its most controllable nature. It is more reliable than the method used by Lord Kelvin in which a coil is positioned between 2 magnets. When the coil passes a current, it causes the coil to move between the 2 magnets, in the case of the siphon recorder. The inkjet gunbody uses the concept of Reighleigh instability, or the phenomena that when a fluid drops, its instability causes the stream to turn into droplets. When the fluid is falling, the stream starts making slight sinusoidal waves which are mirrored from the center of the stream to the edges.

Modern day CIJ printers use piezoelectric crystals to create mechanical waves which are forced into the streaming fluid within the gunbody, creating induced sinusoidal waves and amplifying that minima and maxima with the intensity of the pressure created. The minima creates cut-offs in the stream to create droplets. Electrodes then charge the droplets on their way through the gunbody, which is used to determine the position of the droplet on the substrate and electromagnetic deflectors are used to move the droplets to its intended position. [12,13]

Drop on demand is another type of inkjet printing technique which is more used than the CIJ technique. There are two different types of DoD inkjet printing which differ with how they eject the ink. Thermal DoD uses heat to create a bubble inside the inkjet head. This bubble ejects the ink out of the nozzle and with the added effects of the vapor condensing and the ink's surface tension, ink is pulled from a reservoir to refill the inkjet head and repeat the process. The only requirement for this type of printing is that the ink needs to have a volatile component in order for the rapid vaporization to occur that creates the bubble. The inks would usually have pigment or dyes in them to create the color. Due to the fact that there was no need for any special materials within the printer itself, creating the printer for this type of inkjet printing is very low in cost and labor. Thermal drop on demand became the staple printer for the office and the average home because it was so cheap. This idea was created at around the same time by two different groups, a team working with Hewlett-Packard and a team working at Canon in 1977-1978. The two groups did not collaborate and were completely unaware of each other's work until a few years later.[14,15]

The other method used to eject the ink is the use of piezoelectric materials to expand and contract, causing an increase and decrease in pressure and thus, the ejection

and the refilling of the inkjet head. Because the ink is forced out of the inkjet head by piezoelectric materials, there is no "volatile substance" restriction to the ink like thermal drop on demand has as well as not having a problem with ink residue build up. The drawback is that piezoelectric materials make this type of printing more expensive.[15]

1.2.4 Smartphone Applications

Smartphones have become an invaluable tool for data acquisition, with its ability to take photos while having all the features of a phone. This paired with the incorporation of smartphone apps have given scientists and programmers a way to progress in the field of sciences, tailoring smartphone applications to the specifications needed to be used by the scientists. Smartphones first hit the market in 1994 when IBM and Bellsouth developed the Simon Personal Communicator. This device was a combination of a mobile phone as well as a personal digital assistant, having both the receiver and transmitter of a phone and the operating system of a computer allowing for calling as well as a means of running programs.[16,17] Phone applications started with small functions, such as the calculator and a calendar but saw rapid expansion as phones became cheaper, the battery life increased, and the service providers more capable. Due to the increasing demand for these mobile phones, so did the demand for more applications increase which was not able to be met by the mobile phone developers with the mobile phones of that day. Mobile phones at the time had low resolution screens, limited storage, and minimal processing power. A wireless application protocol or WAP was used in order provide a standard to allow the phones to have a connection to the internet and be within the constraints of the phone and its capabilities. This connection to the internet allowed the user to have a portal where they can access entertainment and informational services found on the internet and avoid having direct access to the device, putting the mobile

phone developers at ease. Eventually, the capabilities of these mobile phones did not meet the demands of the consumers even with the establishment of the WAP in place. WAP site developers could not tailor their sites to specific devices, regardless of how advanced one device is over the other. The user experience was also very cumbersome. The user interface's typing mechanic was a poor fix for allowing the typing of texts, having to use a numeric keypad to enter in long site URLs to access the internet content. Poor processing power was also an issue, as it would take long amounts of time for a small amount of text from a WAP site to be processed and appear on the screen which would be a very expensive endeavor having been billed per second of downloading. Phone manufacturers soon fell behind and were forced to open their phone design, allowing for the development of mobile phone operating systems to enable phones to be able to process faster and allow for more intensive graphical usage of the phone, what we know now today as modern smartphones. In 2007, Apple would release the IOS for their iphones, thus starting their chapter in the fast growing market of smartphones.[17]

1.2.5 RGB and Digital Cameras

The RGB, or red-green-blue, color model is seldom used in the scientific world but due to its integration in the roots of the digital imaging world, it is often used in other applications. Because digital cameras use RGB to determine the color of each pixel, it is the optimal method for analyzing pictures that would be taken by a smartphone application as well as being sufficient enough for sensory applications, due to the human vision operating in RGB. RGB is a way to model colors using a mix of three primary colors, red, green, and blue. The RGB number values of a picture indicate the intensity of each type of color per pixel. This is achieved in digital displays by having 3 lights, one of each color, closely spaced so that from the short distance from the display, the colors

from the three individual color sources spatially overlap due to diffraction of light. At normal distances of viewing, these different lights are indistinguishable to the human eye and become one light that is a mix of the other lights intensities and combined with thousands of other pixels on an array display recreates the image.[18] Capturing this RGB image with a camera is a different process however. When a digital camera takes a picture, it opens up what are called photo-sites, where photons are captured during the time of exposure and are afterwards counted to determine the brightness of that photo-site. Because this process would only create a grey image, a color filter array needs to be implemented. This array will filter out 2/3 of the photons coming into each site, one site filtering out green and blue, another site filtering blue and red, and another site filtering out red and green. The most common filter used is the Bayer filter. Developed by Bryce Bayer, an inventor working for Kodak, this filter takes into account the human eye is more receptive of the color green more than twice the amount of blue and red combined. His filter contains twice the amount of green photo-sites than red or blue and has the red and blue sites alternating down the array. Because of the increase in green photo-sites, the image had more of the light that the human eye is sensitive to and appears clearer with more details. The image you get through the Bayer filter is tinted green so to recreate the proper image. Demosaicing, an algorithm that translates the different color values for every pixel into a recreated pixel color that matches the original image, is used. This produces the final digital image of the original picture. [20]

1.2.6 Optical Properties

The sensory Q-R Codes that were developed are heavily reliant on their optical properties, specifically their absorption in the red spectral region. From Maxwell's

equations for electromagnetic, one can derive the wave equation from which the time-independent, Helmholtz equation can be derived.[21] Helmholtz equation is denoted as

$$\nabla^2 U + K^2 U \qquad \textbf{(1.1)}$$

Where U is the amplitude of light, ∇^2 is the Laplacian, and K is the wave number. The wavenumber includes an imaginary party which represents the attenuation of light as well as the real part which represents the phase change of the light as it propagates through the medium. K is related to the complex refractive index through.

$$K = \beta - j(\alpha/2) \qquad \textbf{(1.2)}$$

Where $\beta = 2n\ r/\lambda$, is the real part of the wave number which is related to the real refractive index and α is the power absorption coefficient

The plan wave solution to Helmholtz equation can be written as

$$U = U0 * \exp(-jKz) \qquad \textbf{(1.3)}$$

Where z is the thickness of the medium, The complex number representation of a propogating wave in equation 3 includes both changes in the phase of the wave as well as the damping of the wave's amplitude with propagation distance z. By multiplying the amplitude of the wave by its complex conjugate $I = |U|^2$, one can form an expression for the intensity of a plane wave that passes through a medium:

$$I = Io * \exp(-\alpha z) \qquad \textbf{(1.4)}$$

where I is the intensity of the light, and Io is the initial intensity of the light before it reaches the medium. As the light wave propatates through the medium, the intensity of the wave decreases due to the absorption coefficient.

Chapter 2

Experimentation

In this chapter, three main experimental topics are described: (1) the formulation, printing, and curing of the various inks used in the Q-R code, (2) the Q-R code reader Iphone app and (3) the spectral analysis of the RGB images. In the first part, the ink formulation and chemistry is detailed for chloroform-based and water-based PCDA ink. Required preparations for the inkjet printing of these inks as well as black ink for the Q-R codes are summarized. Parameters for the inkjet printing of the formulated inks are detailed and described. In the second part, the Q-R code app source code is provided, as well as a detailed description on how the code works. Directions on how to utilize the app is explained as well. In the third part, the spectral analysis of the RGB images is detailed as well as the methodology for processing the data.

2.1 The Inks

2.1.1 Preparing the Chloroform Based Ink

Other researchers have prepared polydiacetylenes in numerous ways, tailor fitting to the specific task that they would need the PDAs to perform, from films of PDA, to PDA vesicles, to the creation of nanocomposites. In this research, processing the chloroform-based ink is described as detailed in Appendix A. Several different densities of PCDA to chloroform were tried. 133.3 ml of chloroform to a gram of PCDA, 200 ml of chloroform to a gram of PCDA, and 40 ml of chloroform to a gram of PCDA were used to test the effects of different densities on printing quality. The 40ml of chloroform to a gram of PCDA was found to be the best of the concentrations, in terms of final print

quality. After stirring, red blobs of what is the residual PCDA can be seen floating in the solution. After the PCDA in the chloroform has been stirred, the solution is put through an 11um paper filter to separate the residual PCDA from the working ink. The chloroform solution that is sifted through the filter is the finished chloroform based ink and the deposits in the paper filter are then disposed. The finished print will show as a thin white powdered film on the substrate. Once the samples have finished being printed, they are UV treated with 254nm light for about 60 seconds to polymerize the PCDA, leaving it a dark blue color.

2.1.2 Preparing the Water Based Ink

Processing the water based ink is slightly different than the chloroform-based. The PCDA is still put into the chloroform and magnetically stirred to ensure as much of the PCDA is dissolved into the chloroform as possible. The density of the PCDA in the chloroform is unimportant in this process, due to the fact that all the chloroform must be dried out before the PCDA can be used. 20ml of chloroform was found to be enough chloroform to fully purify the PCDA and was the amount of chloroform used to decrease the time it takes to dry the purified PCDA. After mixing the PCDA, the solution is then filtered by an 11um paper filter in order to remove the residual PCDA that has not been purified. This residue shows in the form of red globules in the clear liquid. Once the solution is filtered, it is put into a dark refrigerator and set to dry. The refrigerator is used to lower the ambient temperature, slowing the drying process and allowing for better crystallization of the PCDA. The fridge must be dark to avoid pre-polymerization before the intended time of use. Once dried, a white powder, with some yellow on the tips of the crystals is present. This powder is ground in a mortar and pedestal until the powder is as fine as can be possibly made mechanically. Two grams of the purified PCDA powder is

put into a vial, along with 20% its weight in pure Triton X-100 as a surfactant and 15 ml of deionized water. The Triton X-100 that was used is diluted in water with a concentration of 0.02grams of Triton X-100 to 1 ml of water. This density means that 2 ml of this Triton-water mixture contains enough Triton X-100 to be 20% of the wt of the PCDA that was used. Metal beads are put into the vial and the vial is then sealed. This vial is put into a spit-like device that will turn the vial and mix the solution overnight to make sure that the surfactant and PCDA are as homogeneous as possible in the water. The PCDA mixture is probe sonicated for 30 minutes before its use. The probe should be set to sonicate for 30 seconds with 15 seconds of rest in between to allow for the solution to cool. After being deposited onto the substrate, the design is UV treated with 254 nm light for 45-60 seconds to reveal the deep blue design.

2.1.3 Preparing the Black Ink

The black ink does not require the purification that the PCDA based inks do. However, it still needs to be filtered before use in the inkjet printer or else the inkjet printer will clog. 4ml of the black ink is mixed with 2ml of deionized water to promote faster filtration while still maintaining the ability to provide a dark print. The same 11um filter paper was used to filter the black ink.

2.2 Printing

2.2.1 Inkjet Printing

Figure 2.1 Dimatix Inkjet Printer.
Source : [21]

Ink-jet printing is a type of fabrication method that involves the deposition of materials onto a substrate. Because of the nature of ink-jet printing, it does not require a clean room and can be used even in households. The printer that was used is the drop on demand (DoD) Dimatix DMP-2800 series material printer. This device works by applying a potential difference across the 16 nozzle heads, located at the bottom of the ink-jet cartridge. The particular nozzle head that was used during the printing process has a nozzle size of 20 microns. Applying a higher voltage to the nozzle will increase the force that the piezo electric material will induce onto the ink. Too much voltage will result in the ink splashing and reduce resolution due to the unintentional spreading of the ink. Too little voltage however, and the ink may stick to the nozzle head, to be cleaned off during the cleaning cycle and never make it to the substrate, or possibly not even leave the nozzle head. The DMP-2800 materials printer's stage is auto calibrated to be level upon start up. The image that is printed is created by the printing program, called Dimatix Drop Manager. These patterns are made through a series of different sized

rectangles, where the start of the rectangle is specified in the x and y directions, and the size of the rectangle is specified to determine the dimensions of the rectangle to be created. A special features are included with this ink-jet printer to allow for more control over the printing process, which include being able to control the plate temperature on which the substrate is placed on. This feature can help with the drying process, causing solvents to evaporate at a faster rate and leave the material behind for the next layer to be deposited on top of the precious one instead of spreading because the ink is still wet. It also works to anneal other types of inks during the printing process. Another feature is the ability to control the amount of layers to be printed, allowing for the production of thick films or even layers of different materials. More features include the ability to adjust the distance the nozzle is from the plate while printing. This allows for printing on thicker substrates but having too large a distance from the substrate will cause the same effect as having too much voltage and create splashes of the ink and a decrease in resolution. The ability to control how many of the nozzles are in use during the printing process is also given. Printing with more of the nozzles allows for shorter printing time but printing with fewer nozzles coupled with sharpening the angle of the inkjet nozzles, which can be done simply by turning the stage that the inkjet head is clipped onto, can allow for finer detail and higher resolution of the design.
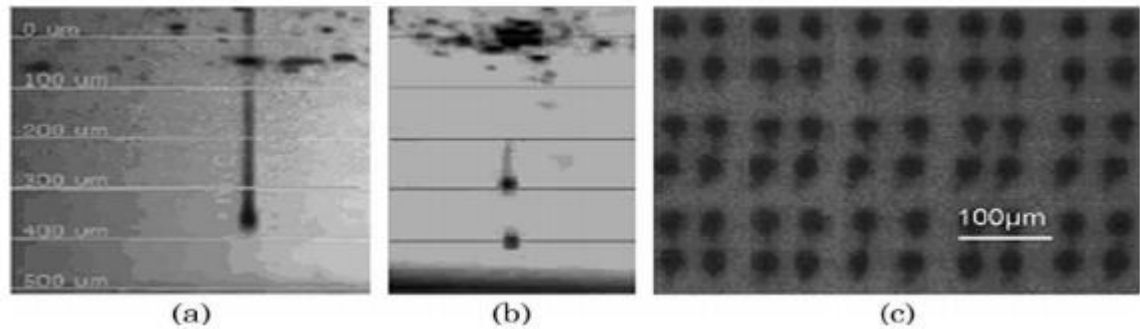
Figure 2.2 Image taken by the built-in camera of the deposition system shows the droplet with (a) a perfect drop and (b) a split droplet due to the incorrect waveform setting. (c) Image of the deposition resulting from the split droplet, in which a secondary small dot is formed next to the main drop.
Source : [22]

2.2.3 Printing Preparations

The stage is cleaned with a pad and isopropyl alcohol to rid any dust or particles on the stage that would cause the substrate to not lay flat. The Dimatix material cartridge, model #DMC-11610, is altered by cutting its locking mechanism off with a razor, so that the inkjet head can be taken off freely and the cartridge itself refilled when need be. Any old cleaning pad in the machine is taken off and a clean one is then locked into place. The substrate is aligned with the boarders that are etched into the stage and taped down to prevent movement of the substrate during printing. The stage that the inkjet head is clipped onto is adjusted to 12.5 degrees from the x axis, allowing for a finer distance between subsequent nozzle lines, creating a sheet of ink. Using the Dimatix Drop Manager, the pattern to be printed is designed and saved as a computer file. After creating the pattern design and selecting it, one can select how many layers of each are printed for each design going, which is dictated by the type of ink. The location of the design on the substrate material is entered into the printer software, as well as spacing between subsequent patterns. Unlike the layering and nozzle voltage, the spacing is not

altered between the different inks used. The inkjet head is set to spray using 25 volts for the black ink while the chloroform based ink as well as the water based ink are set to spray at 23 volts because they are a less viscous solution. The substrate, which is your typical office style printer paper, is measured to be around 100um thick, so the ink-jet head nozzle is set to 115um to be 15um above the printer paper to prevent the ink from splashing during ejection. The chloroform ink is set to print out 10 layers thick, while the water based being a lighter density of PCDA, must be printed out with 40 layers. The black ink, being the darkest of the inks being used, only needs to be printed with 5 layers. The cleaning cycle is locked at 10 bands or times printing across the substrate. For an added measure of making sure the substrate is laying flat on the stage, the vacuum pump is put on which sucks air through several periodic holes in the stage.

2.3 Testing

2.3.1 Heating the Samples

Figure 2.3 The Lab Companion OV-12 vacuum oven. Picture taken from Cole-Parmer online catalog, Item # UX-52402-96

The oven that was used to heat the samples is the Lab Companion OV-12 vacuum oven. The vacuum feature for the oven is neither necessary nor used. However, the device provides precise control of the temperature to which the sample is exposed to, compared to typical ovens that use a heating element which is within the oven causing temperature differentials within the oven's volume. The oven is heated to the intended temperature and given five minutes for the temperature to stabilize. Ten samples are put in at a time and kept in the oven for 30 seconds. The samples are then taken out and recorded on the phone application. The temperature is then increased by fire degrees Celsius and the same ten samples are put back into the oven and given another 30 seconds. This process repeats itself until the final intended temperature. During this heating a set of ten samples that have not been heated are put in along with the ten samples that were already being heated. Both sets of samples are taken out and recorded.

The oven turned off to cool to show that heating the samples repeatedly is equivalent to heating the samples once to a final temperature.

2.3.2 The Phone App

The photos taken during the heating of the samples are taken with fluorescent ambient lighting. The camera is pointed at the design and is held still at around six inches away until it is able to find the best focusing. The app was written by an undergraduate student (Thomas Lombay) and tested on the Q-R code sensors developed as part of this Master's Thesis. If the app is able to read the Q-R code, the design is outlined in yellow, showing the area that will be computed by the color analyzing section of the phone app code as well as the entire section is outlined in blue. If there is no highlighting, the phone app has not registered that there is a Q-R code to read and will not take a picture until a Q-R code is found and the screen is tapped. These sections are what are evaluated by the phone app. Once these outlines are achieved, the screen on the Iphone is tapped to take the picture. The picture that was taken is shown with the information processed by the app underneath it, showing the message that is encoded into the Q-R code, the color changing part of the Q-R codes color, whether it is red, blue, or indeterminate, as well as the calculated temperature. The program calculates the temperature by comparing the picture to samples that were used as models during the programs encoding. These pictures are saved for later use during the RGB analysis. The RGB analysis as well as a discussion of the findings for the RGB analysis can be seen in section 2.3.3.

Two samples made from the chloroform ink which are reserved from the samples that would be tested in the oven, are used to test the apps capabilities. One of the samples has not been heated whereas the other one is heated to above 140C on a hot plate to

ensure that the code is fully changed to its red phase. The samples are first illuminated by the ambient light of the lab, which is fluorescent. Ten pictures of each sample are taken under these conditions, approximately six inches away from the sample and records are taken of what temperature the app reads the samples to be, the color that the app perceives the samples to be, and if it correctly read the Q-R code message.

The testing protocols are designed to assess the versatility of Iphone app under different sample orientation and illumination. The Testing protocols for the chloroform samples and for the water-based samples are the same and can be summarized as follows

1: Effect of Illumination conditions

a: Test samples using Iphone app under fluorescent, incandescent, dark, and natural lighting illumation conditions.

-Can the code be read? What color does the app read the sample to be? What temperature?

2: Effect of sample orientation

a: Test all samples using Iphone app as sample is rotated.

-Can the code be read? Does it affect the color reading?

Figure 2.4 The angle test set-up as well as the fluorescent ambient light test set-up.

As seen in Figure: 2.4, the sample, during the angle test, is placed on a turning dial that has degree markings on it to indicate how much the dial has turned. This dial turns around the entire way, making it easy to zero the dial for any experiment. The entire experiment is set up in a room that is completely lit by fluorescent light bulbs.

For the fluorescent light test, the samples are placed at 0 degrees and a picture is taken of a blue sample and then a red sample. Each sample is recorded with the app ten times and then the results are recorded manually in a notebook. This same process is done again, this time for incandescent light. The set up for this test can be seen in Figure 2.5
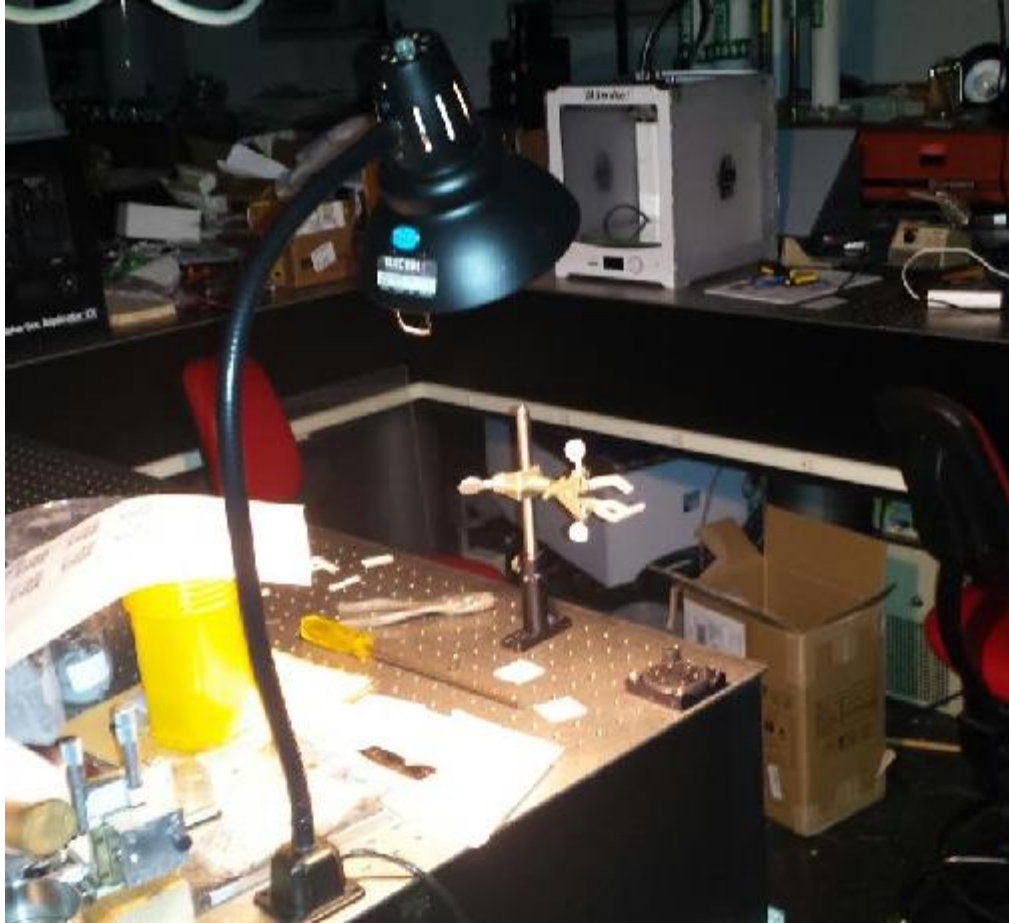
Figure 2.5 This set up uses an incandescent light bulb shined directly onto the sample.

As shown in Figure 2.5, All outside light sources are turned off so the only light is purely incandescent. The lamp is placed across the set-up from the tester's location to eliminate shadowing. The dial from the angle test is kept as a stage to keep the samples the same distance from the camera. The sample is placed on the stage so that the edges of the square paper are as close to either vertical or horizontal as possible and the color changing portion of the design is kept in the top left corner of the design with respect to the phone's camera view of the design.

Figure 2.6 The low light level ambient light test set up.

For the low illumination test, the camera holder as well as the sample stage is kept in the same area as the previous tests. The entire set-up is covered from all but one side from light by cardboard boxes. The side that is not covered is for access to the set-up to tap the camera and take the pictures. The set up is placed where the only light source is behind the opposite side of the set up from the open side to eliminate direct light from getting to the set up, leaving only reflected light from other surfaces. This will cut the amount of light getting to the sample dramatically while still providing possibly enough light for the camera to process the picture. The same process used during the fluorescent and incandescent lighting conditions is used, where ten pictures are taken from while the phone is being held by the clamp.

Natural lighting is the final illumination test for the app, where the samples are brought outside during a day. The forecast during the testing was mostly cloudy, which

limited the amount of light reflecting off of the samples, causing glares. The samples are placed on level ground and ten pictures of each sample are taken and the information recorded.

2.3.3 RGB Analysis

The RGB analysis is being used to get a more detailed color analysis of the samples as well as having a separate color analysis to compare to the phone app. The digital pictures taken during the heating process as well as a digital picture taken before the heating started are put into a program called ImageJ, an open-source processing program designed for scientific multidimensional images. This Java-based program comes with several features, including the ability to display, edit, analyze, process, save, and print images that can range from 8-bit color images and grayscale images, to 16-bit integer images and 32-bit floating point images of various formatting types including jpeg, gif, bmp and others. A section of the picture that is inside the color changing area is selected, taking care to leave as much of the not printed on area, as well as the black ink sections out.

An area is analyzed by ImageJ and the RGB measurements are displayed as the average intensity of each color throughout the selected section. A section of the substrate that was not printed on, that is within close proximity to the color changing section of the QR code, is selected after each RGB measurement to measure the background light and the ratio of background light to light from the colored section is calculated to measure the percentage of light that is absorbed by the color changing section, which should eliminate any difference in illumination from sample to sample. The substrate was chosen to be white printer paper, due to the white of the paper being able to reflect red, green, and blue

equally, because the white background would make the design more prominent in color, and because it is a cheap material both in cost and easy to procure.

2.3.3 Ink Rub Test

It was noticed that there is a large variability in the RGB values from sample to sample in both the chloroform-based ink and the water-based ink. One possible cause of this is that the ink was not printed to be optically thick. An optically thick design would decrease the amount of light that is being bounced, straight from the substrate to the camera, leaving only the data from the ink film itself. In the opposite limit of an optically thin sample, a portion of the illuminating light would propagate through the ink and be reflected by the substrate material, consequently distorting the reflected color. Moreover, the reflected color for an optically thin sample would depend on the thickness of the ink. To test this theory, a PCDA powder rub was created using the steps from Appendix D. The ink is taken in its powdered form and rubbed onto four pieces of filter paper until a thick coating of the powder covered the center of the filter paper. A white label is placed on a table as a background reference. Because the ink is rubbed onto the filter paper, the Iphone app cannot take a picture of the blobs so pictures of the samples are taken with a Samsung Galaxy S4 smart phone. The pictures are taken next to a white label that was put onto the desk to act as a background. A piece of aluminum foil is folded several times to be made thick, and is then flattened onto a hot plate using a large piece of cardboard. The hot plate is then turned on and a stick thermometer is made to lay over the hot plate, with the bulb of the thermometer touching the aluminum plate, using a binder clip. The hot plate is heated up past the intended temperature, and the hot plate is then turned off. The intended temperatures are 40, 50, 60, 70, 80, and 90 degrees Celsius. The temp is monitored until it reaches the intended temperature. Each sample is placed on top of the

aluminum plate and pressed down using the cardboard from earlier and is given 20 seconds to be heated before it is removed, and the next sample placed on the hot plate. Once all four samples are heated, the samples are recorded via pictures again and the hot plate heated to the next intended temperature. Once all the samples have been recorded, the images are opened in the ImageJ program and the RGB spectrum of the centers of the ink blots as well as the center of the white label are recorded.

Chapter 3

Results

3.1 Phone App Testing Results

3.1.1 Ambient Light Test
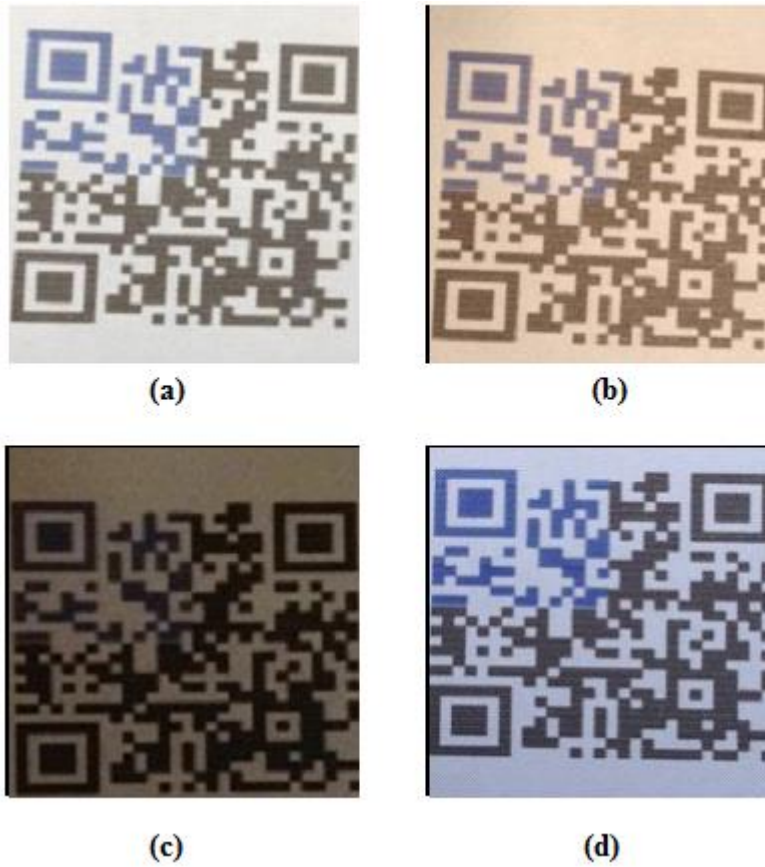
Figure 3.1 Samples from the ambient light test for the blue-phased samples. (a) Fluorescent light (b) Incandescent light (c) Low light environment (d) Natural light
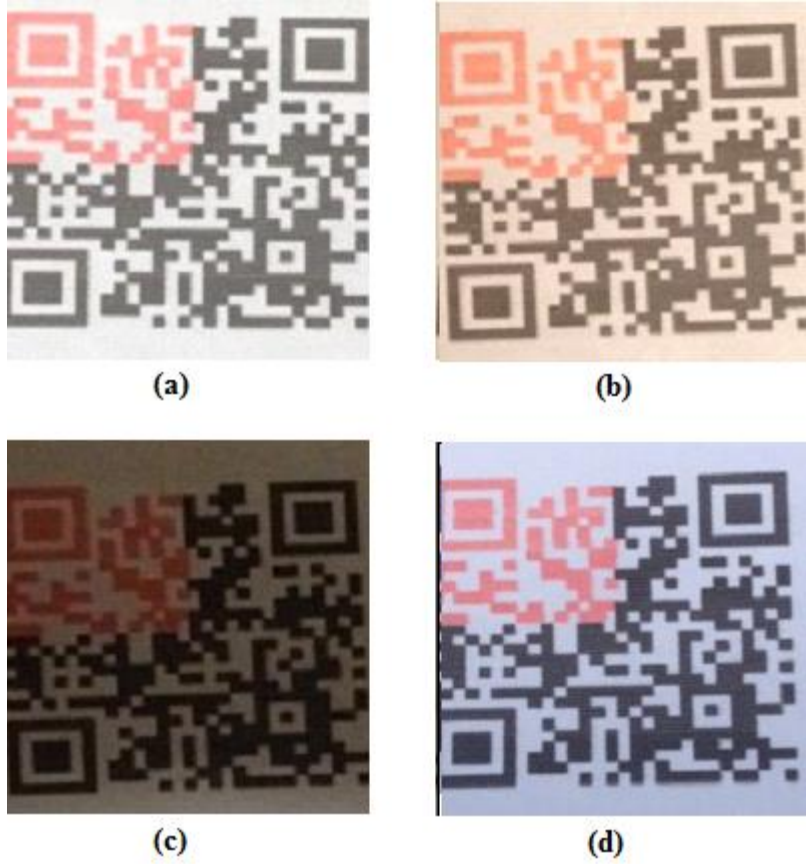
Figure 3.2 Samples from the ambient light test for the red-phased samples. (a) Fluorescent light (b) Incandescent light (c) Low light environment (d) Natural light
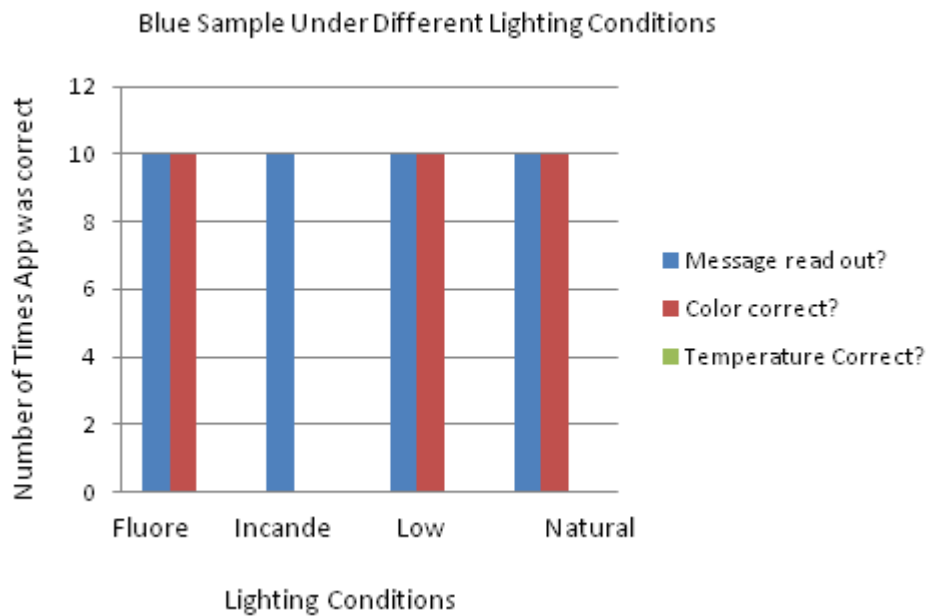

Figure 3.3 Graph of the performance of the Phone App under different lighting conditions for the blue sample. The graph shows the number of times the app read the message right, read the color correctly, and read the temperature correctly.
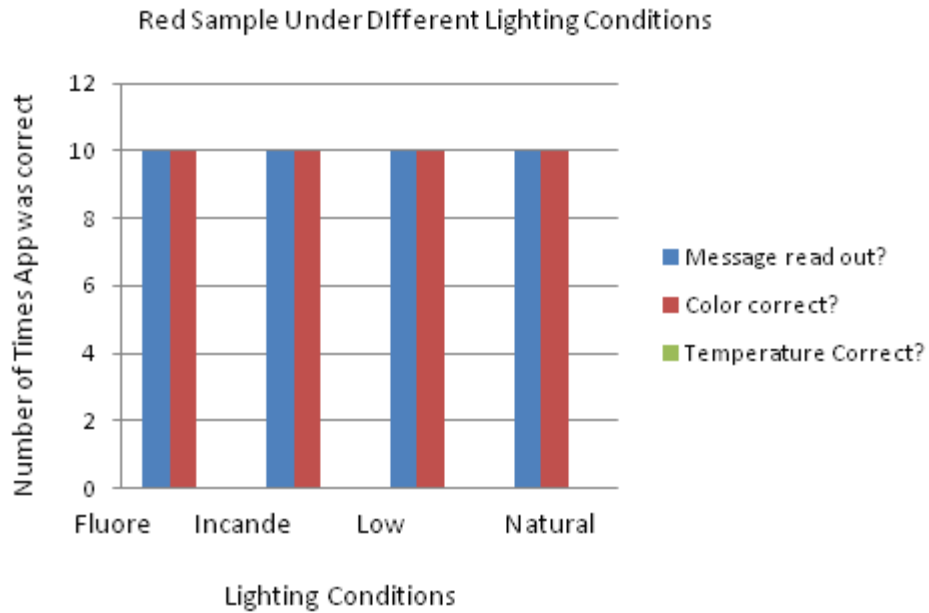
Red Sample Under Different Lighting Conditions

Figure 3.4 Graph of the performance of the Phone App under different lighting conditions for the red sample. The graph shows the number of times the app read the message right, read the color correctly, and read the temperature correctly.

As can be seen in Figure 3.3 and 3.4, the fluorescent lighting environment provided almost perfect results, where the correct color is read as well as the message read out. The reading of the temperature was off however, which always read as 30 degrees Celsius.

The incandescent light proved to be a less effective lighting condition compared to incandescent light. All blue samples were read to be indeterminate in color; however for both the red and the blue sample, the message was displayed properly. The incandescent light was also able to determine the red samples color with 100% accuracy for the ten samples.

The low lighting condition yielded the same results as the fluorescent lighting condition, where all samples are read properly and their color displayed correctly but the temperatures are read to be 30 degrees Celsius for both the blue and the red samples.

Natural lighting provided the same results as the fluorescent and low lighting illuminations. This shows that the phone application is capable of reading the app under many lighting conditions, as long as the light source is providing pure white light. The purity of the light coming from incandescent light is not enough to allow for the app to read properly.
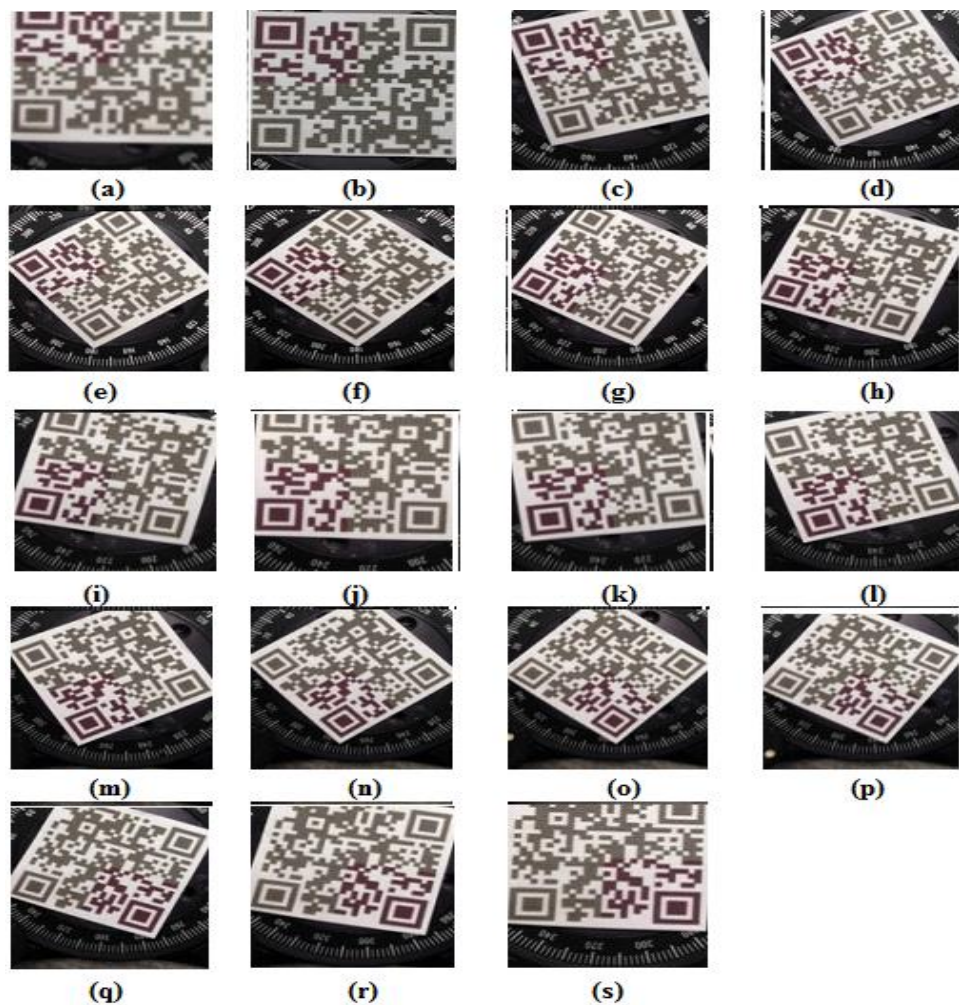
3.1.2 Angle Test

Figure 3.5 The angle test done with a sample in purple phase under fluorescent light. (a) 0 degrees (b) 10 degrees (c) 20 degrees (d) 30 degrees (e) 40 degrees (f) 50 degrees (g) 60 degrees (h) 70 degrees (i) 80 degrees (j) 90 degrees (k) 100 degrees (l) 110 degrees (m) 120 degrees (n) 130 degrees (o) 140 degrees (p) 150 degrees (q) 160 degrees (r) 170 degrees (s) 180 degrees.

Figure 3.6 The angle test done with a sample in red phase under fluorescent light. (a) 0 degrees (b) 10 degrees (c) 20 degrees (d) 30 degrees (e) 40 degrees (f) 50 degrees (g) 60 degrees (h) 70 degrees (i) 80 degrees (j) 90 degrees (k) 100 degrees (l) 110 degrees (m) 120 degrees (n) 130 degrees (o) 140 degrees (p) 150 degrees (q) 160 degrees (r) 170 degrees (s) 180 degrees.

The app is able to take a picture of the code from 0 to 180 degrees, however this is under optimal conditions. When the app is being held in hand however, the app had the capability to take a picture up to 50 degrees from the vertical in the positive and negative direction. The shaking of the camera causes the app to not be able to focus on the design

and highlight it for processing. This shows that the angle at which the phone can be held and take a reliable picture is dependent on how steady the operator can hold their hand.

3.2 RGB Results

3.2.1 Chloroform

The results from the ImageJ RGB analysis was found to be a more descriptive analysis of the color of the samples than the Iphone app, which can only display whether the sample is red, blue, or unable to be determined as you can see in Figure 3.13 and Figure 3.21. After uploading the pictures onto ImageJ, the averaged RGB intensities vs, the background light intensities of the selected region are plotted in the following figures for the red, green, and blue values.
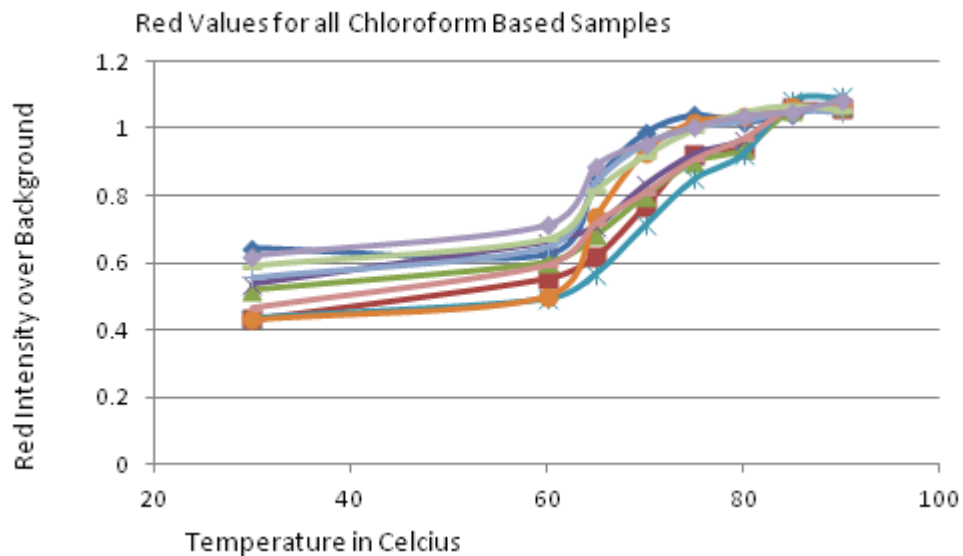

Figure 3.7 The values for all red intensities of the sample versus the red intensity of the background. The values for the temperature start at 30 degrees Celsius and end at 90 degrees Celsius.
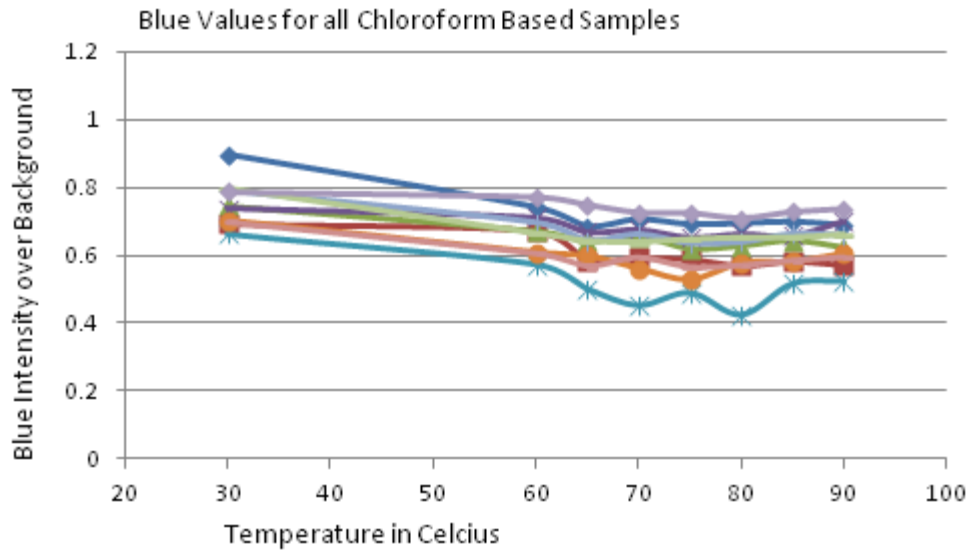
Figure 3.8 The values for all blue intensities of the sample versus the blue intensity of the background. The values for the temperature start at 30 degrees Celsius and end at 90 degrees Celsius.
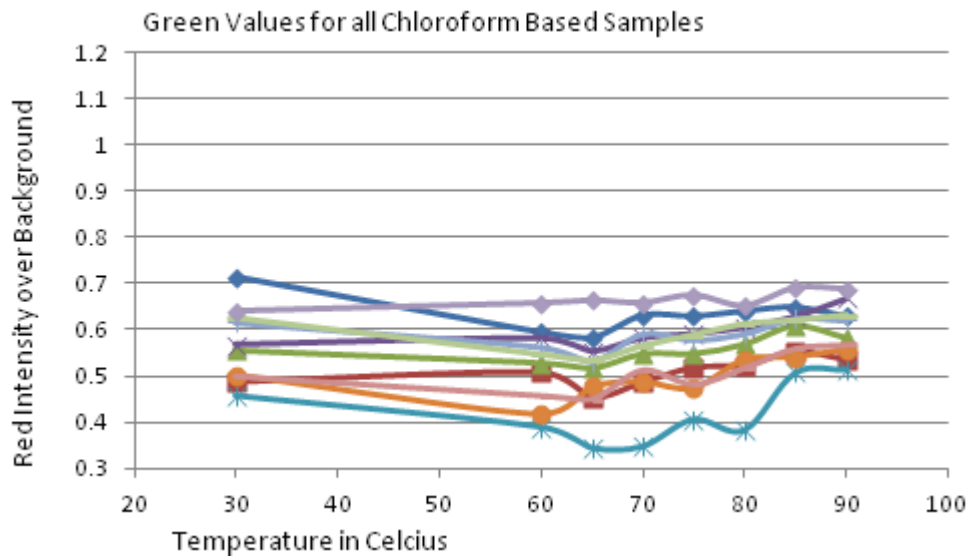

Figure 3.9 The values for all green intensities of the sample versus the green intensity of the background. The values for the temperature start at 30 degrees Celsius and end at 90 degrees Celsius.

As seen by Figure: 3.7, red intensity ratios for the chloroform-based inks start to increase, indicating its initiation of the transition to the red phase, between 60-65 degrees Celsius while the increase in this ratio levels off after 85 degrees Celsius. The samples seem to have a very wide spread in terms of reflectance, ranging from around 20% all the

way up to almost 70%, which can be seen in the red RGB values. The values for blue between all the samples seemed to slightly decrease upon the sample starting to change color. This change then levels off around 70 degrees Celsius and then fluctuates slightly around its final ratio, between 45% to 75% of the background intensity. Green seems to be the most consistent with its intensity values over the range of temperatures to which it is exposed, slightly increasing as the temperatures get higher. The green values, like the other 2 colors, share an intensity spread of around 30%. It is noticed that at 90 degrees Celsius, the spread of the data is very narrow compared to the rest of the data, possibly indicating that there is some unevenness in the samples that manifests in a difference in color during heating but ending at the same max value where the heat is high enough to fully change all the samples regardless of these unknown differences.

The following figures are an attempt to create an equation for the color changing data taken from the chloroform-based ink data. With the creation of an equation that fits the data accurately, it would be possible to only have the RGB values and be able to give an interpretation of the temperature.
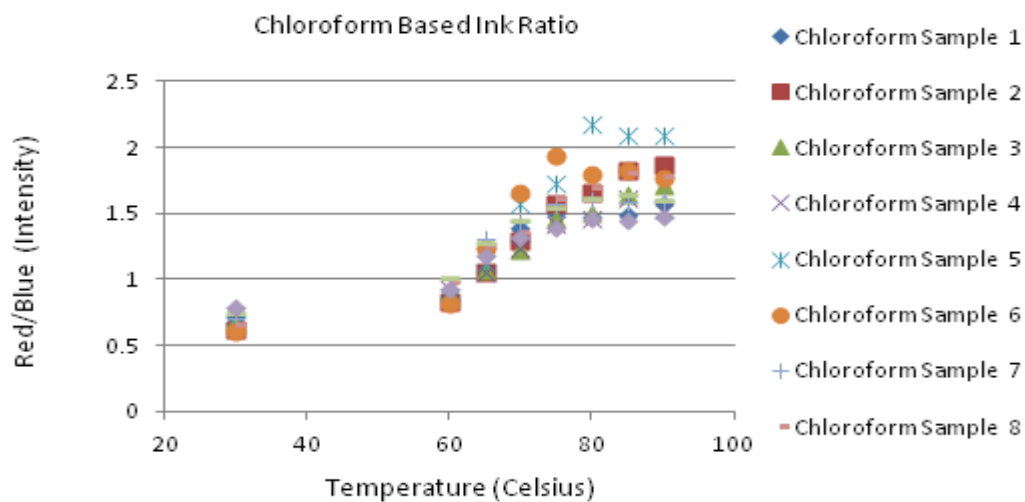

Figure 3.10 A graph taken from the chloroform ink data. The graph shows the intensity of the red RGB values divided by the intensity of the blue RGB values.
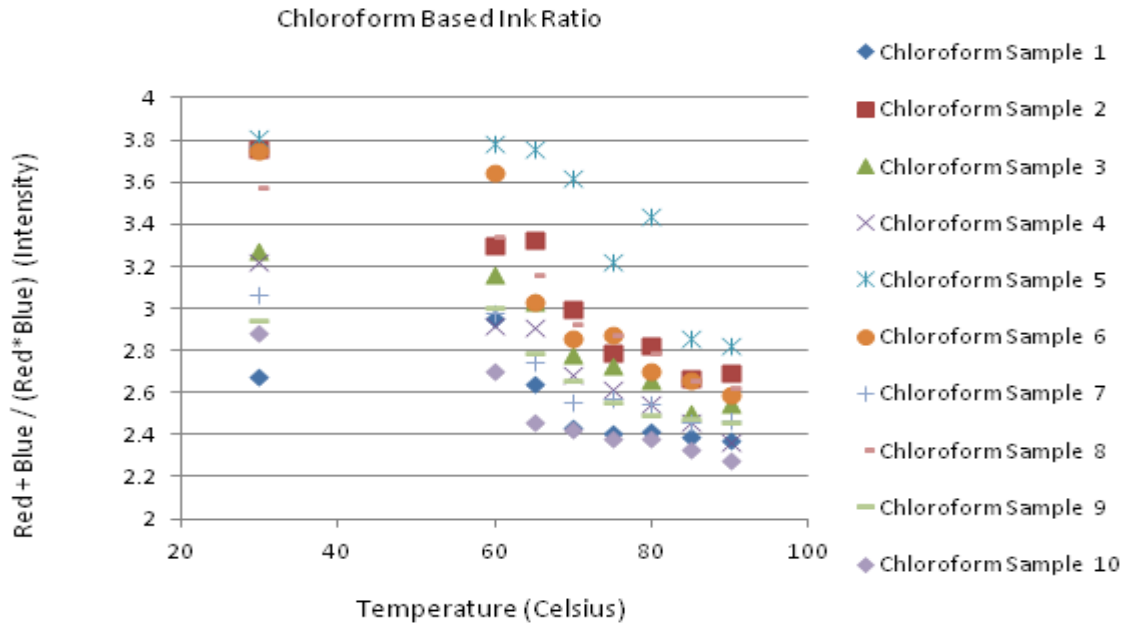
Figure 3.11 A graph taken from the chloroform ink data. The graph shows the intensity of the red RGB values in addition with the blue RGB values and divides the sum by the multiplication of the red and blue RGB values.

As shown in Figures 3.10 and 3.11, the data is highly variable. The data appears to have less variability in the red intensity divided by blue intensity graph of the chloroform based ink at low temperatures, but gradually gains more and more variability as the temperature is increased.

Figure 3.12 One of the chloroform based ink samples through different stages of its transition. Starting from the top left going right are the pictures at (1) 30 degrees Celsius (2) 60 degrees Celsius (3) 65 degrees Celsius (4) 70 degrees Celsius (5) 75 degrees Celsius (6) 80 degrees Celsius (7) 85 degrees Celsius (8) 90 degrees Celsius. You can clearly see the purple phase that is between the blue and the red phase take place from (2) and (6), spanning around 20 degrees Celsius.
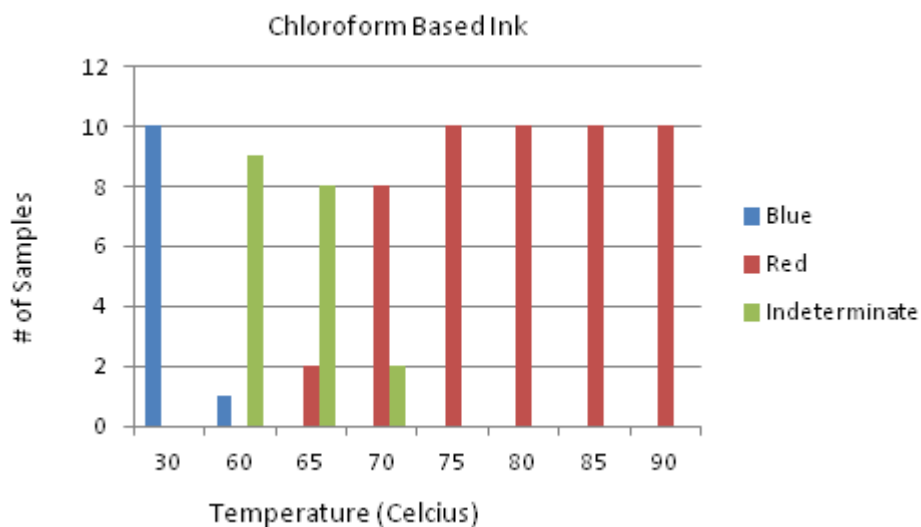
Figure 3.13 The results of the chloroform based ink test with the phone application. The app testing of the chloroform based ink solutions are done with the pictures from Figure 3.12 as well as the other samples taken by the process described in section 2.3.1. The figure describes how many samples at a certain temperature read as red, blue, or indeterminate from temperature ranges ranging from 30 to 75 degrees Celsius.
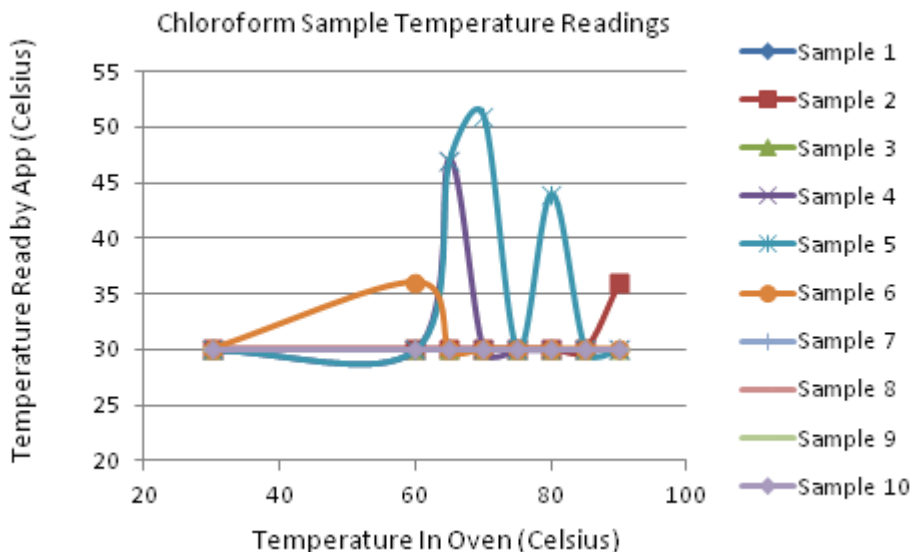

Figure 3.14 Temperature read out for 5 samples from the Chloroform based ink.

The Iphone application appeared to have difficulty determining the color of the samples between the temperatures of 60 to 70 degrees Celsius. Most of the difficulty appears to be with the blue color, showing that around 60, only 1 sample was determined to be blue whereas at 70 degrees Celsius, 80% of the samples were determined to be red. Below 60 degrees Celsius and above 70 degrees, the samples are read as either red or blue, making a threshold type sensor from these chloroform inks. The phone app repeatedly read the temperature to be 30 degrees Celsius regardless of the temperature to which the sample was exposed, with a few other temperatures. The temperature code part of the app appears to not be working.

3.2.2 Water-Based

Just like the chloroform-based ink, the water-based ink images are loading into ImageJ and their average R, G and B values for the sample compared to the background intensity values within a selected region are shows in the following figures.
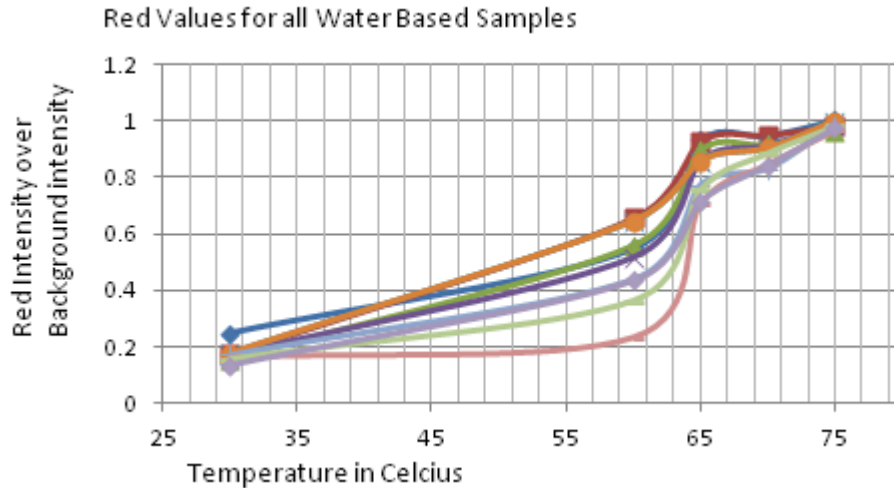

Figure 3.15 The values for all red intensities of the sample versus the red intensity of the background. The values for the temperature start at 30 degrees Celsius and end at 75 degrees Celsius.
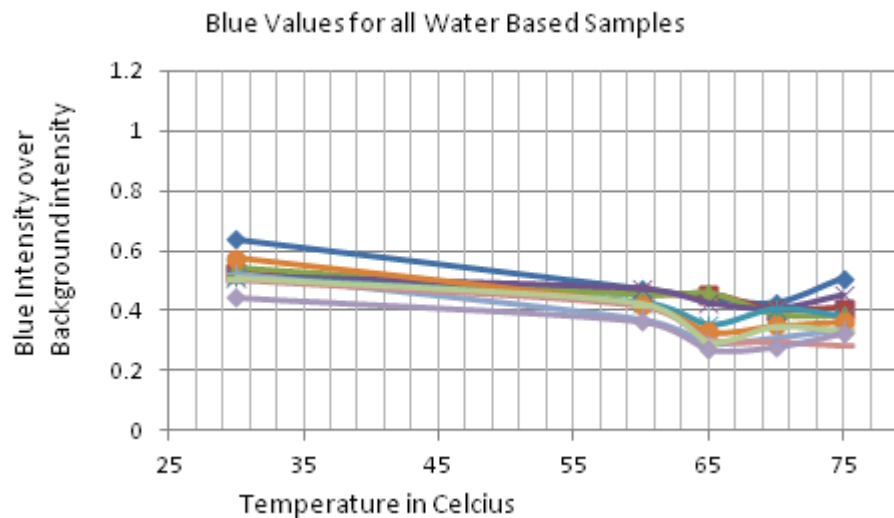

Figure 3.16 The values for all blue intensities of the sample versus the blue intensity of the background. The values for the temperature start at 30 degrees Celsius and end at 75 degrees Celsius.
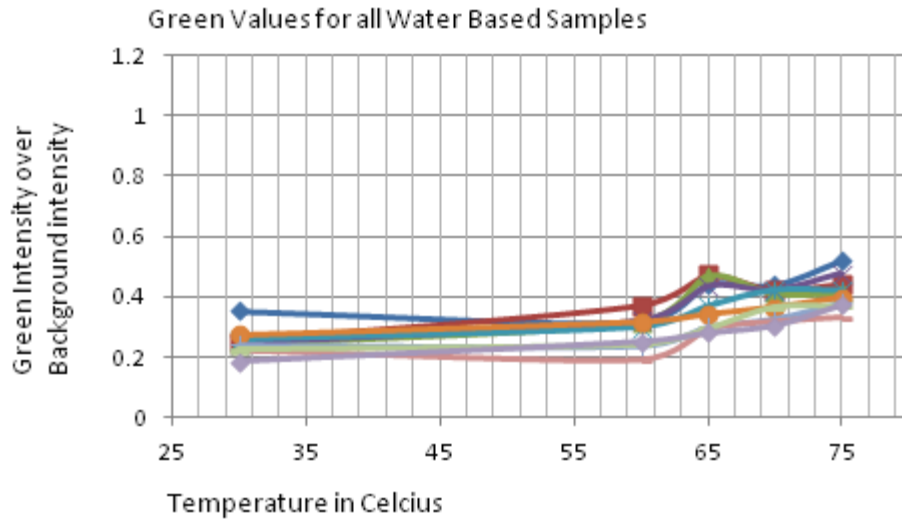
Figure 3.17 The values for all green intensities of the sample versus the green intensity of the background. The values for the temperature start at 30 degrees Celsius and end at 75 degrees Celsius.

As you can see in Figures 3.15, 3.16 and 3.17, there is a slight decrease in spread for all temperature values compared to the chloroform ink in Figures 3.7, 3.8, and 3.9, except at 60 degrees Celsius in the red, where the spread of the reflectance values differs from around 25% to 70% reflectance. The transition region also appears to be narrower than the chloroform ink, creating less "indeterminate" area which can be seen in Figure 3.13. Several attempts at finding an equation that fits the water based ink's data were tried. Having an equation that the data follows may help with temperature acquisition by the phone app as well as being able to use the RGB values to figure out a temperature from the data. The following figures were the results.
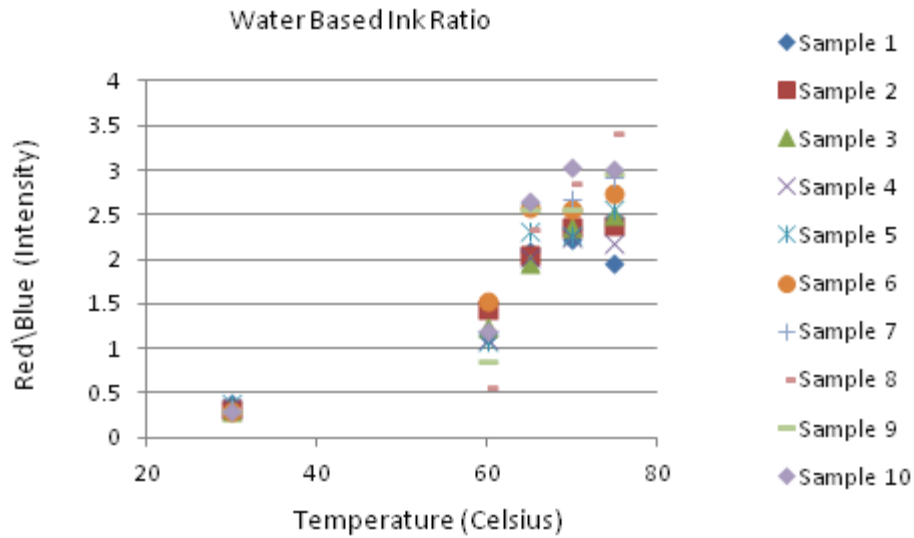
Figure 3.18 A graph of the water based ink data. The graph shows the effects of temperature on the values for the red intensity divided by the blue intensity. The high amount of variability makes the fitting of the data to an equation, with useable accuracy, difficult.
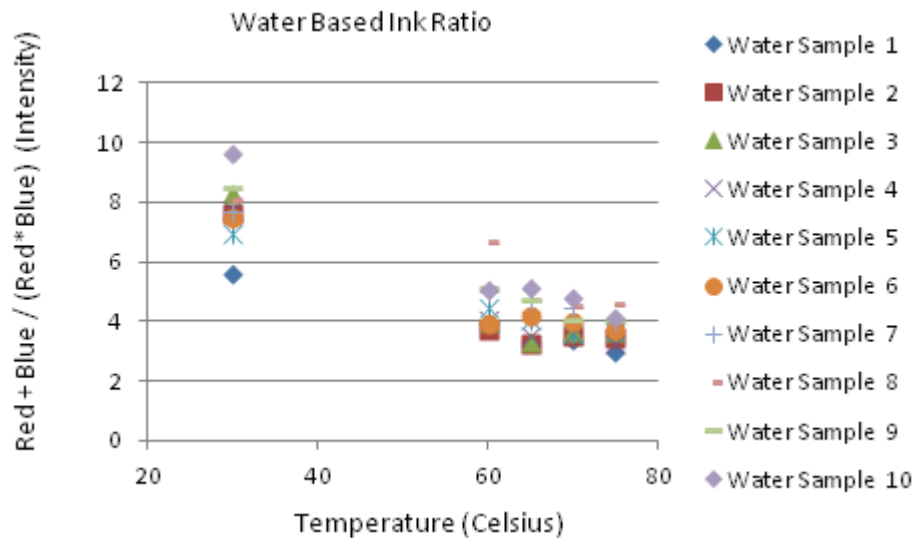

Figure 3.19 A graph using the data from the water based ink RGB values. This graph shows the addition of the red and blue values divided by the the multiplication of those values. The data from the graph shows that there is still a high variability in the data and would not be able to accurately determine a temperature from any given RGB values.

Figure 3.20 One of the water based ink samples through different stages of its transition. Starting from the top left going right are the pictures at (1) 30 degrees Celsius (2) 60 degrees Celsius (3) 65 degrees Celsius (4) 70 degrees Celsius (5) 75 degrees Celsius. The samples existence in the purple phase is very short, spanning shortly before 60 degrees Celsius and ending before 65 degrees Celsius.
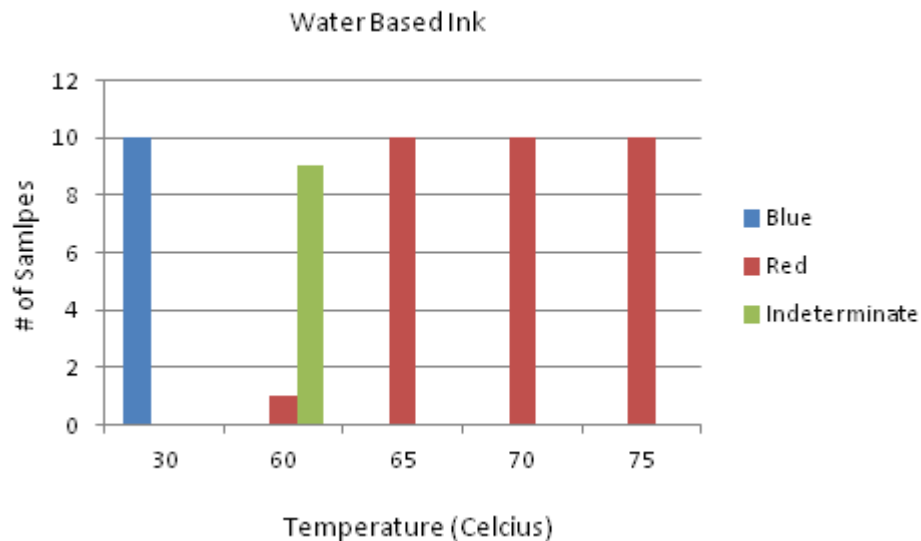

Figure 3.21 The results of the water base ink test with the phone application. The app testing of the water based solutions are done with the pictures from Figure 3.20 as well as the other samples taken by the process described in section 2.3.1. The figure describes how many samples at a certain temperature read as red, blue, or indeterminate from temperature ranges ranging from 30 to 75 degrees Celsius.
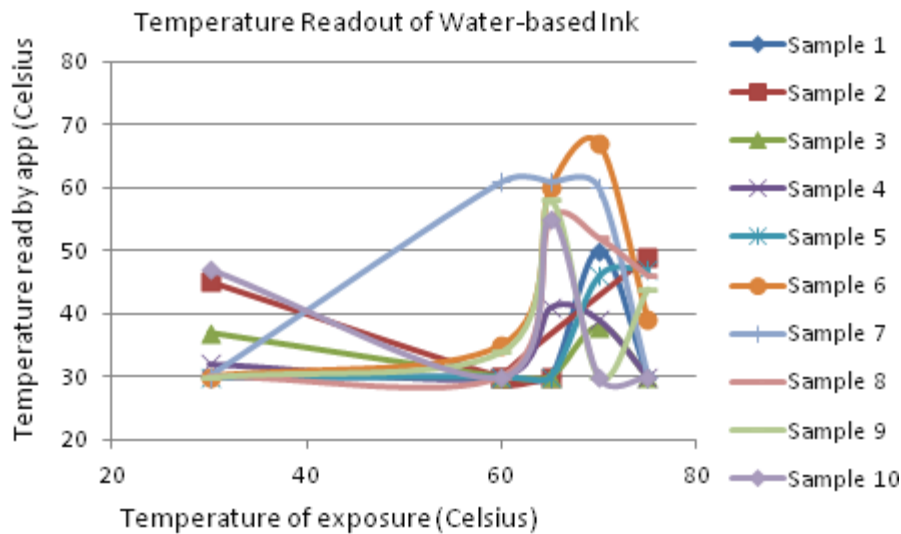
Figure 3.22 The temperature read out of the phone app for five samples from the water-based ink.

As discussed before, the indeterminate region in the water-based solution is a lot smaller than in the chloroform ink creating a more reliable threshold sensor than the chloroform-based solution. It's also noticed that at 60 degrees, the water based solution had one sample that was registered as red whereas in the chloroform based solution, one sample was registered as blue. This could insinuate that the difference in solution causes the transition temperature to change, leaving the question of can you tailor the transition temperature and to what extent can that temperature change? The phone app did not appear to work for the water-based samples, as well as the chloroform-based samples. The water-based samples appeared to have more randomness than the chloroform-based. It is noteworthy to realize that the blue temperature readings has a lot more variance of values than the chloroform-based, where most of the temperature readings read to be 30 degrees Celsius
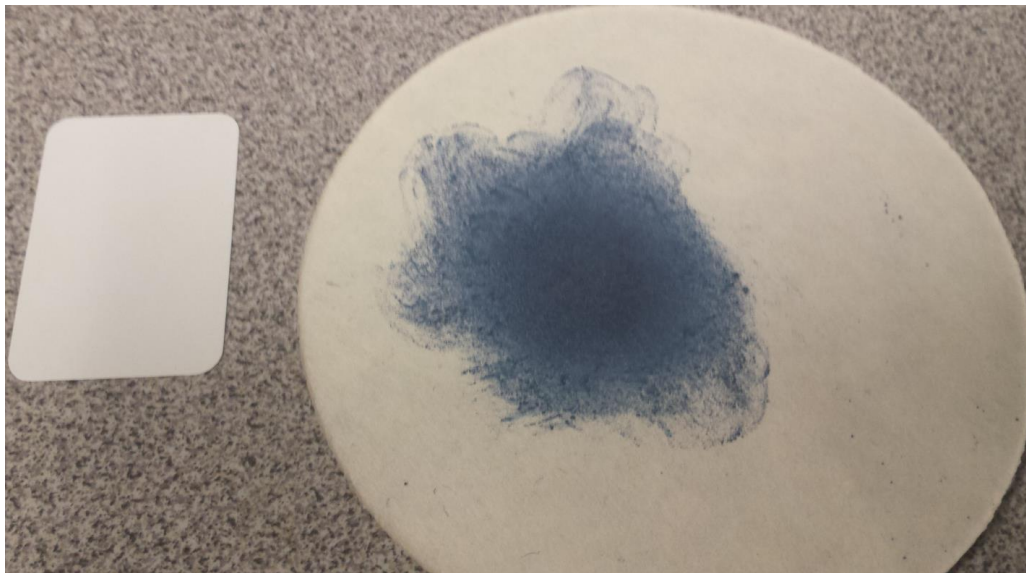
3.2.2 Ink Rub Data

Figure 3.23 A sample of the ink rub set up next to the white label. The ink rub's RGB is evaluated at the center of the ink blob and compared to the white label's RGB value as a means of normalizing the RGB values.
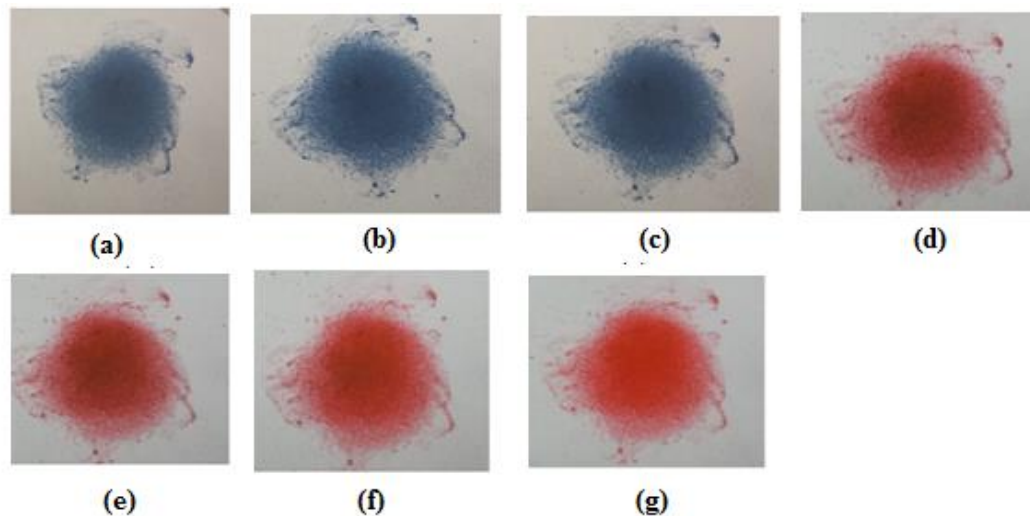
Figure 3.24 One of the ink rub samples through different stages of its transition. Starting from the top left going right are the pictures at (a) 30 degrees Celsius (b) 40 degrees Celsius (c) 50 degrees Celsius (d) 60 degrees Celsius (e) 70 degrees Celsius (f) 80 degrees Celsius (g) 90 degrees Celsius.

It is noticed that the thick coat of PCDA on the filter paper does not go through the "purple phase" that the chloroform and water-based inks go through. At 60 degrees Celsius, it is seen that the ink rub is a lot more "redder" than the chloroform and water

based ink at 60 degrees Celsius. In the following figures, Figure 3.25, 3.26, 3.27 and 3.28, the RGB values for each sample is displayed.

Figure 3.25 The RGB values for Sample 1 during the ink rub test. The figure describes how the RGB values of the first sample changed with the increasing temperature. The temperature ranges from 30 to 90 degrees Celsius
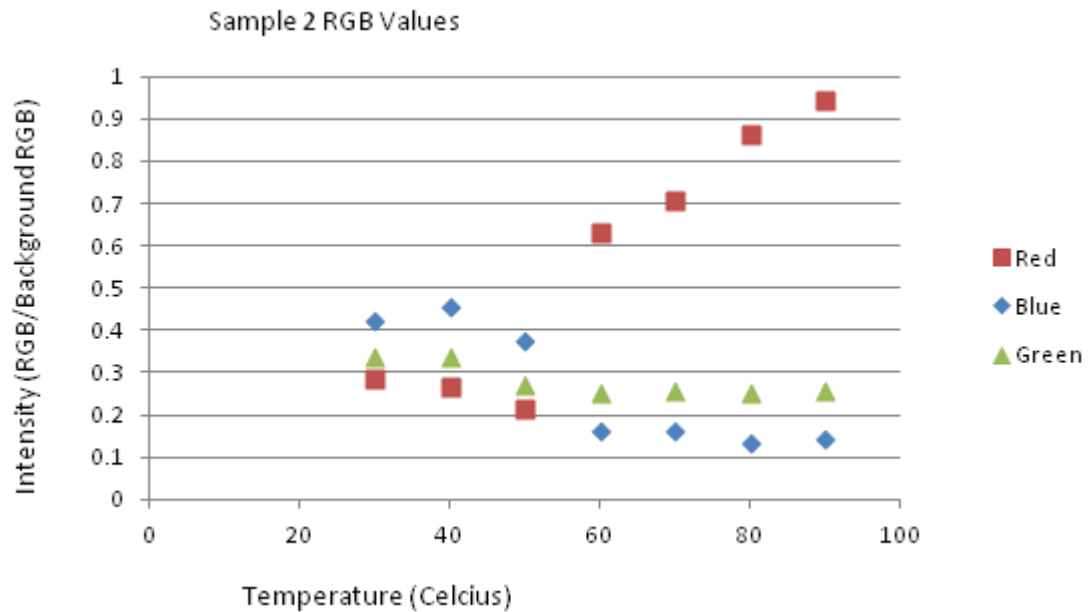
Figure 3.26 The RGB values for Sample 2 during the ink rub test. The figure describes how the RGB values of the first sample changed with the increasing temperature. The temperature ranges from 30 to 90 degrees Celsius
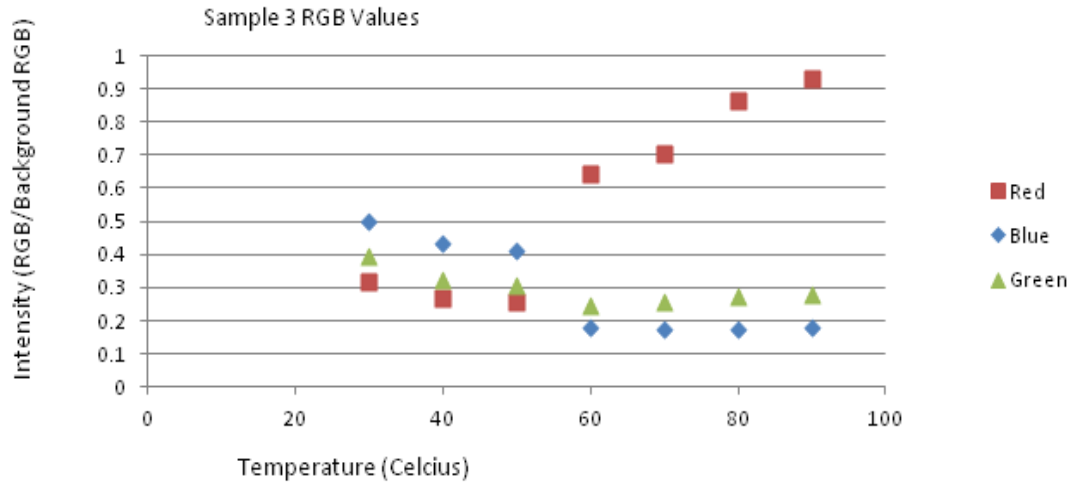
Figure 3.27 The RGB values for Sample 3 during the ink rub test. The figure describes how the RGB values of the first sample changed with the increasing temperature. The temperature ranges from 30 to 90 degrees Celsius
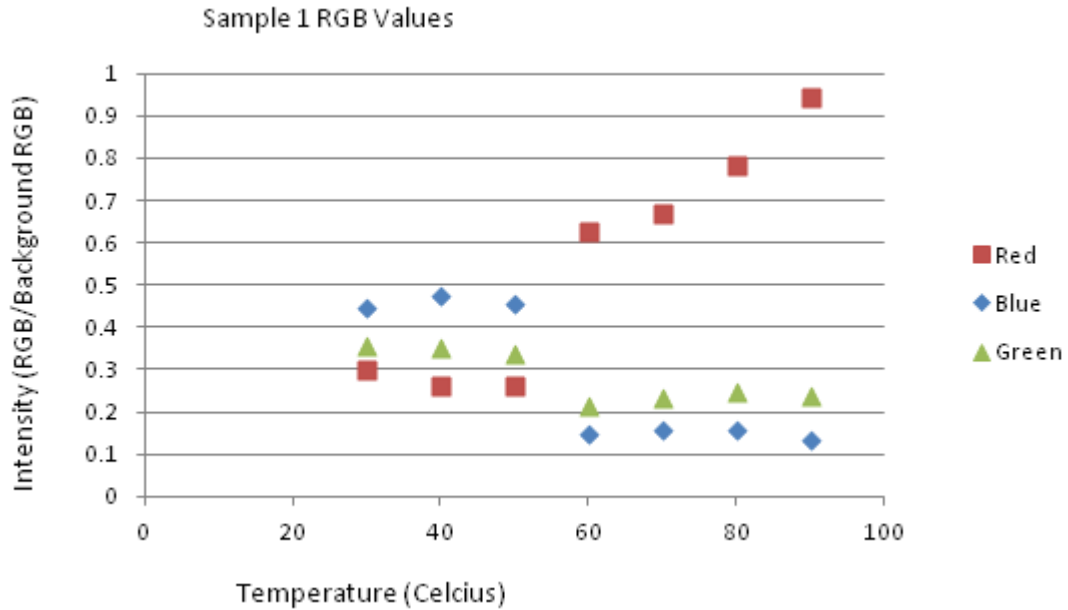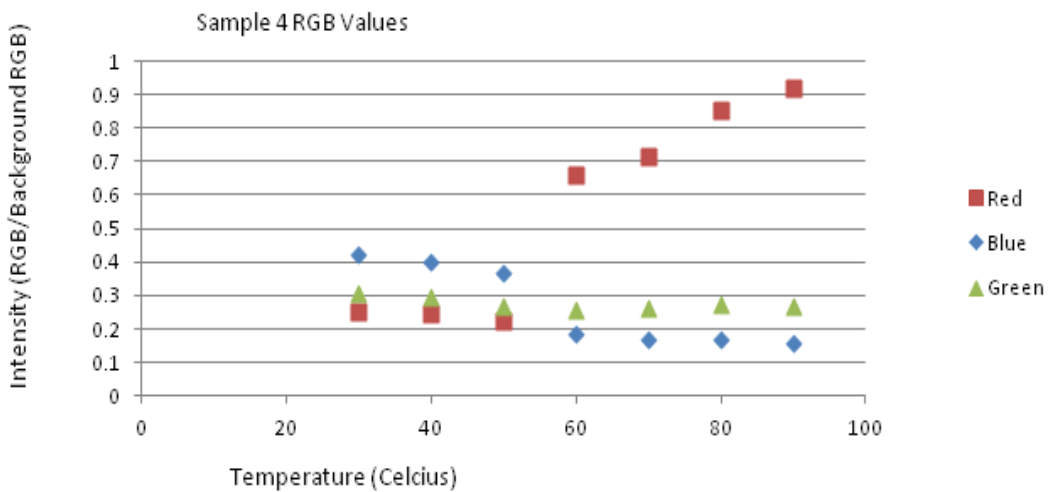

Figure 3.28 The RGB values for Sample 1 during the ink rub test. The figure describes how the RGB values of the first sample changed with the increasing temperature. The temperature ranges from 30 to 90 degrees Celsius

One can see that at 60 degrees Celsius onward, the samples appear to have a linear relationship with the reflectance of the red RGB value and the temperature. After 60 degrees, the blue and green values appear to not change noticeably. In the following figures, one can see the compared color values from sample to sample and the general flow of the data, as well as the spread of the data.

Figure 3.29 The red values for all the samples. The figure shows the spread in red values from sample to sample and how they change with temperature.

Figure 3.30 The blue values for all the samples. The figure shows the spread in red values from sample to sample and how they change with temperature.

Figure 3.31 The red values for all the samples. The figure shows the spread in red values from sample to sample and how they change with temperature.
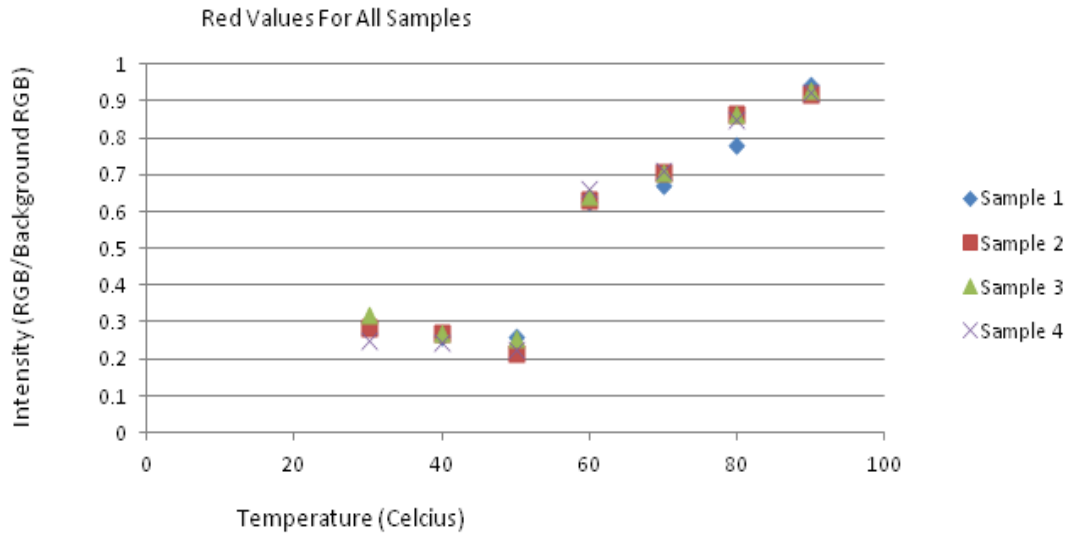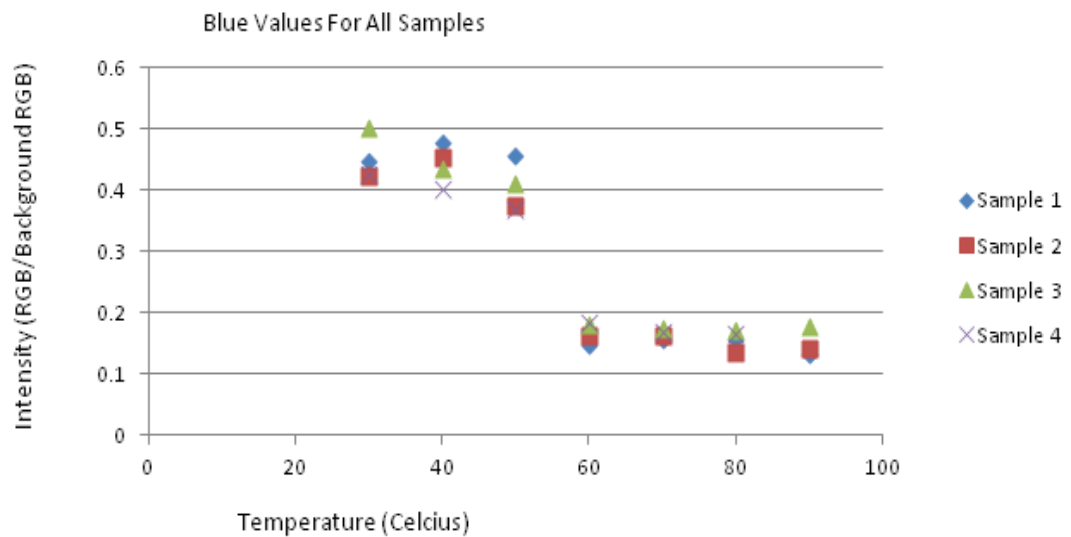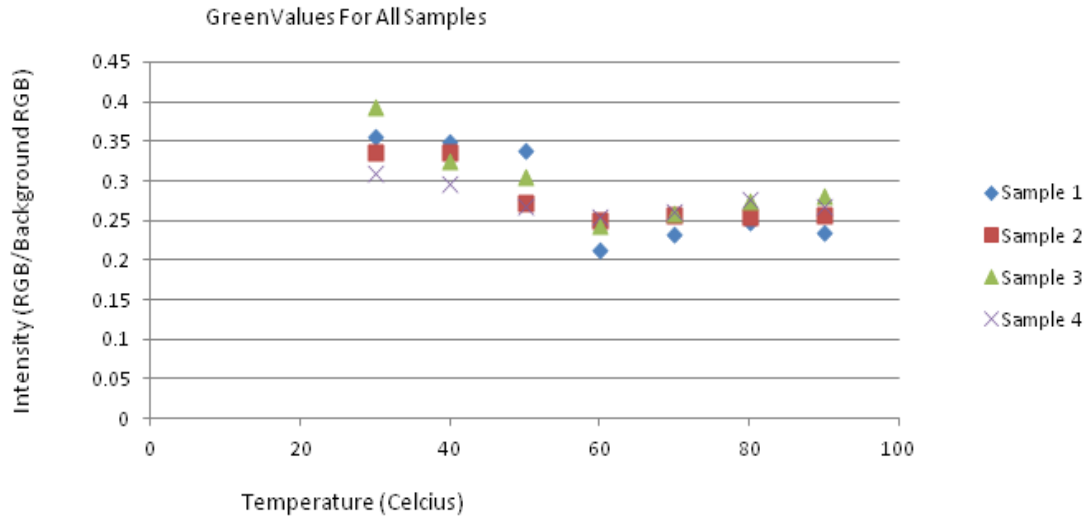
As seen by Figure: 3.29, red intensity ratios for the ink rubs slightly decrease until the transition temperature is reach at 60 degrees Celsius, where the red intensity values greatly increase. The red intensity continuously increases linearly with temperature up until 90 degrees Celsius, almost fitting the equation 1% * (Temp – 60) + 63.5. The spread for the red intensity values at a certain temperature are seen to be less than 10%.

The blue intensity ratios for the ink rubs do not change much until 60 degrees Celsius is reached. The values for the blue intensities then suddenly drop and stay at around 20% with a less than 5% spread in either the positive or negative direction with 25% as the zeroed value. The spread of the blue values are more spread than the red values but still staying under 10%. The spread of the blue values has a smaller spread for the higher temperatures than the blue values from before the transition.

The green values seem to decrease very slightly until it reaches 60 degrees Celsius, then gradually increases at an even slower pace. The spread of the green values stays below 10% at any given temperature, but does not tighten after the transition temperature like the blue values.

In comparing the inkjet printed sensors to the ink rub tests, it is clear that the sample-to-sample variability is significantly reduced with the ink rub samples. Since the ink rub samples are substantially thicker than the inkjet printed sensors, the results suggest that the variability in the RGB colors of the inkjet printed-sensors is probably due to the varying thickness of the optically think inkjet printed sensors

CHAPTER 4

Conclusions

The goal of this thesis is to present an idea for giving a visual indicator of temperature to a Q-R code and prove that it can be read. Several tests were done to quantify the capabilities of both the phone app that is reading the Q-R codes as well as the color changing and printing capabilities of ink used to print the Q-R codes.

4.1 Phone App Tests

The phone app was first tested for its ability to work under varying conditions. The first condition that was tested is the phone apps ability to work under different lighting conditions. The phone app was used to measure two different samples, one that was in the blue phase and one that was in the red phase, in fluorescent, incandescent, low lighting and natural lighting environments. The app worked well in all lighting conditions minus incandescent, where there was trouble determining the color of the blue phase. This manifested in the app reading "Indeterminate" as the color. In all lighting conditions, the app was able to read the message embedded into the code however, it was not able to determine the proper temperature for the red samples. Although there was a high variability in the RGB data, as can be seen in Figure 3.15 -3.17 and 3.7 – 3.9, this does not seem to be the issue with the temperature calculations, because the temperature displayed on the app did not change from the blue to red samples.

Second, the phone app is oriented at different angles to test its ability to capture the Q-R code while not completely vertical. The sample was turned 10 degrees for every picture until it reaches 180 degrees. The phone app was able to capture the code at all angles when being held by a clamp, however, there is a noticeable change in how much the phone can capture when being held manually. During the testing, holding the phone

manually yielded pictures from 0 to less than 50 degrees from the vertical. This indicates the importance of steadiness for the phone app to take a picture as well as showing that the phone app is going to have different capture capabilities from person to person, depending on how steady the person can hold the camera.

The final test done was to test the phone apps, sensitivity to the color change. The samples are heated and pictures are taken every 10 degrees Celsius. As can be seen in Figure 3.21 and 3.13 the phone app has difficulty determining a color during the "purple phase" of the ink. This area of indeterminacy is shortened in the water based ink, only having trouble with a sample at 60 degrees Celsius whereas the chloroform based ink had trouble determining the color between the temperatures of 60 to 70 degrees Celsius. In all temperatures, the ability for the app to read the message embedded in the code was unhindered and was not accurate. This could be caused by samples not being optically thick and the phone is recording the reflections from the substrate as well as the sample.

4.2 RGB Analysis

To acquire a more detailed profile of the color change of the inks, an analysis of the RGB values for all temperatures, was done. The analysis was done by taking the pictures, which were taken from the phone app, and put them into a program called ImageJ. This program allows for the calculation of the average RGB values for a selected region on the picture. These values can be seen in Figures 3.15-3.17 and 3.7-3.9. Although all the graphs followed a general line, the variability of each samples values was very high, averaging around a 30% intensity difference from sample to sample. This difference may be caused by differences in thickness, caused by clogging of the inkjet nozzle during the printing process. It was also noted that the transition temperatures differed from the water-based solution to the chloroform based solution. A reason for this

could possibly be the fact that in the chloroform-based solution, the PDA forms weak complex formations with the solvents, or any organics that it comes in contact with, causing an increase in the transition temperature. These formations are not made in the water based solution so there is no increase in transition temperature, and the transition of the pure PCDA is seen. There is no extensive research to date about this phenomena and therefore lacks explicit examples however, some proof of this can be seen in "Thermochromism in Polydiacetalene –Metal Oxide composites", a paper published in *The Journal of Materials Chemistry.* [23]

4.3 Ink Rub Test

Because the samples are not optically thick, the variances in thickness show as reflections from the substrate itself may have been counted. To test this theory, an ink rub test was done. The inks, in their powdered form, are rubbed onto filter paper to create a thick layer of PCDA. Four samples were made and pictures were taken by a Samsung Galaxy S4 Smartphone. Due to the fact that the rubs are not a Q-R code, the Iphone app that was created would not register the samples, and thus not be able to have their picture taken. These pictures were put into the program, ImageJ, such as the previous RGB testing was done. It was found that the variability was cut down to a 10% spread in data as opposed to the 30% that the chloroform and water based inks provided. Not only was the spread of the data diminished, but the graph took a more linear shape, especially after 60 degrees Celsius was reached. This data confirms that printing the designs with more layers will decrease the variability of the samples.

<div align="center">

Appendix A

Chemistry

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A.1 Chloroform Ink Formulation Steps

-The PCDA was purchased from Sigma-Aldrich: Product number 76492-5G

-The Chloroform was purchased from Sigma-Aldrich: Product number 372978-1L

-Place .25 grams of PCDA into beaker

-Pour 10 ml of chloroform into beaker

-Place magnetic stirrer into beaker and stir for 20 minutes

-Use 11um filter paper to filter solution while pouring into another beaker. Prior
to pouring the solution into the filter paper, the filter paper should be wetted
with chloroform

A.2 Water-Based Ink Formulation Steps

-The PCDA was purchased from Sigma-Aldrich: Product number 76492-5G

-The Chloroform was purchased from Sigma-Aldrich: Product number 372978-1L

-Place .5 grams of PCDA into beaker

-Pour 20 ml of chloroform into beaker

-Place magnetic stirrer into beaker and stir for 30 minutes

-Use 11um filter paper to filter solution while pouring into another beaker. Prior
to pouring the solution into the filter paper, the filter paper should be
wetted with chloroform

-Leave solution in fridge until chloroform evaporates completely

-Take left over white crystals and manually grind with mortar and pestle

-Mix .2 grams of grinded purified PCDA powder with 20% wt of Triton X-100
and 15ml of deionized water

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56

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-Place mixture and metal beads into a closed container

-Attach closed container onto a spit-like device and leave over night

-Pour liquid into another beaker, keeping all metal beads out of the new beaker

-Probe sonicate for 30 minutes

       a) Probe sonication set to 30 second bursts with 15 seconds rest

       b) Probe sonicate at 80% intensity

       c) Place beaker into a larger beaker with water

A.3 Black Ink Preparation Steps

-Higgins magic waterproof ink is ordered from Wayfair Supply: Product number
UBW1079

-Place 4ml of black ink into graduated cylinder

-Pour 2ml of deionized water into graduated cylinder

-filter with 11um paper filter into a clean beaker. Prior to pouring the solution into
the filter paper, the filter paper should be wetted with deionized water

A.4 Ink Rub Formulation Steps

- The PCDA was purchased from Sigma-Aldrich: Product number 76492-5G

-The Chloroform was purchased from Sigma-Aldrich: Product number 372978-1L

-Place 1 gram of PCDA into beaker

-Pour 30 ml of chloroform into beaker

-Place magnetic stirrer into beaker and stir for 45 minutes

-Use 11um filter paper to filter solution while pouring into another beaker. Prior
to pouring the solution into the filter paper, the filter paper should be
wetted with chloroform

-Leave solution in fridge until chloroform evaporates completely

-Take left over white crystals and manually grind with mortar and pestle

-Shine 253nm UV light on powder while stirring with glass rod until all powder
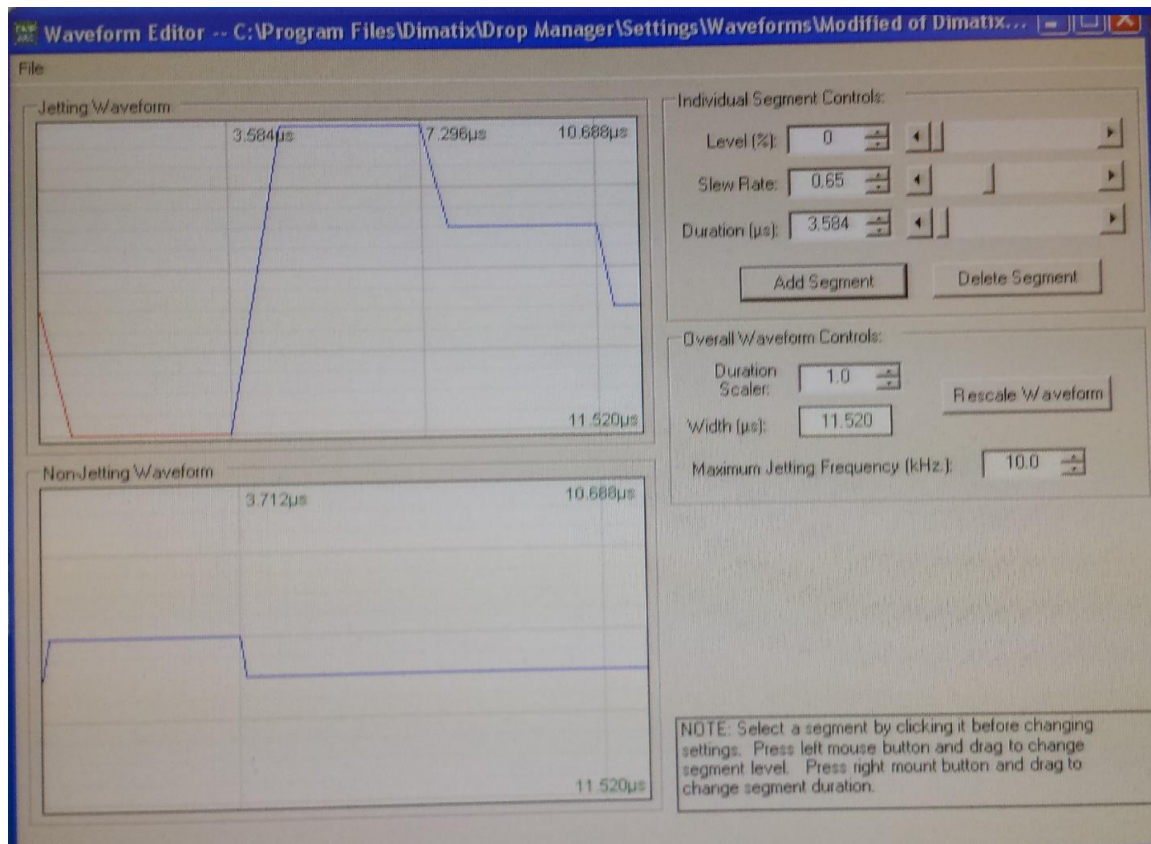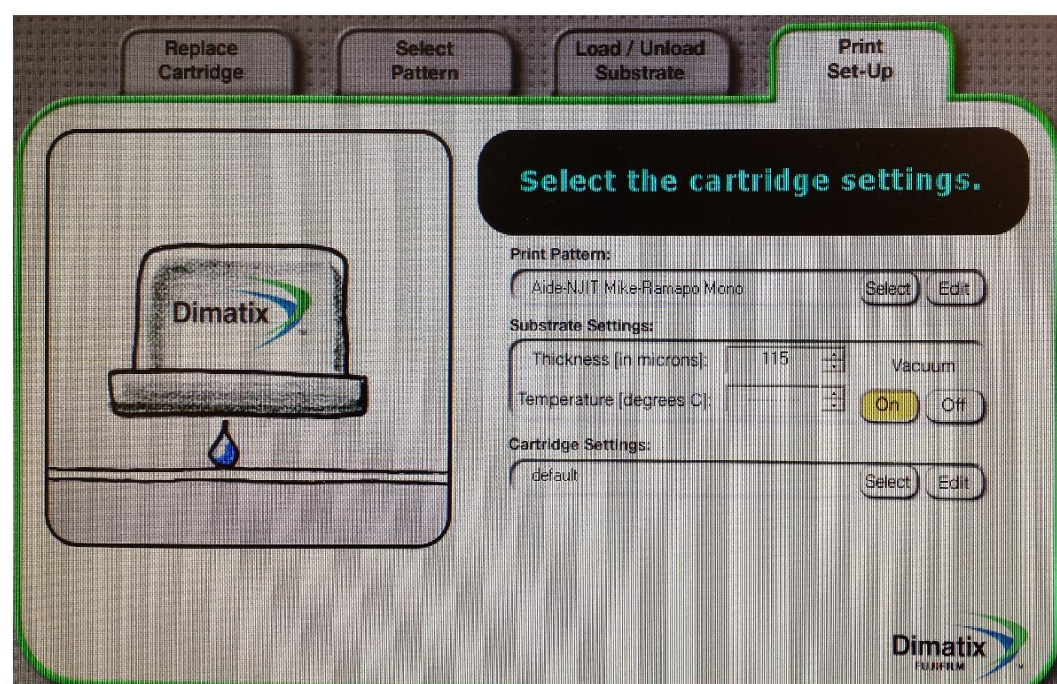becomes navy blue in color

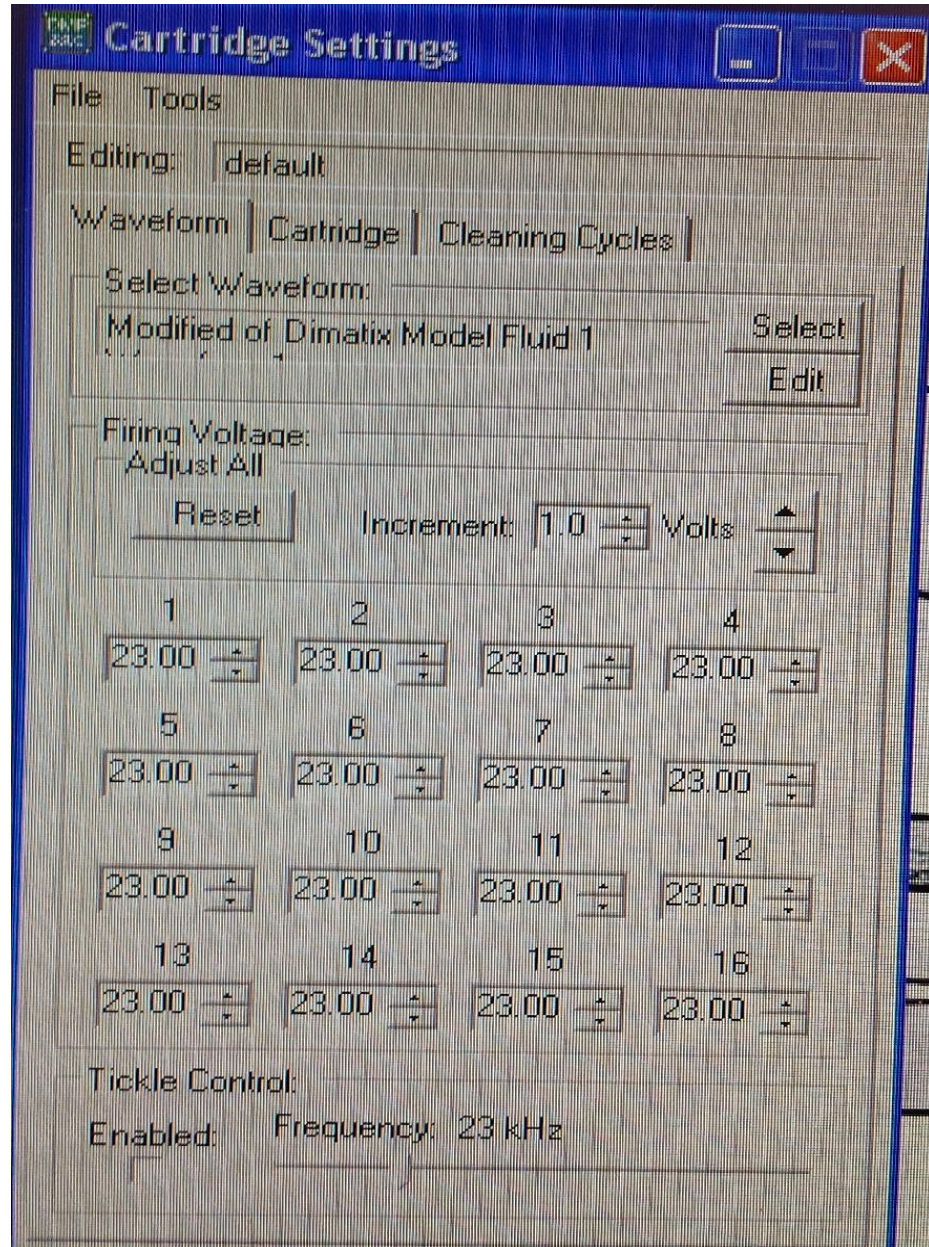# Appendix B

Printer Settings

B.1 Q-R Code Pattern and Layering
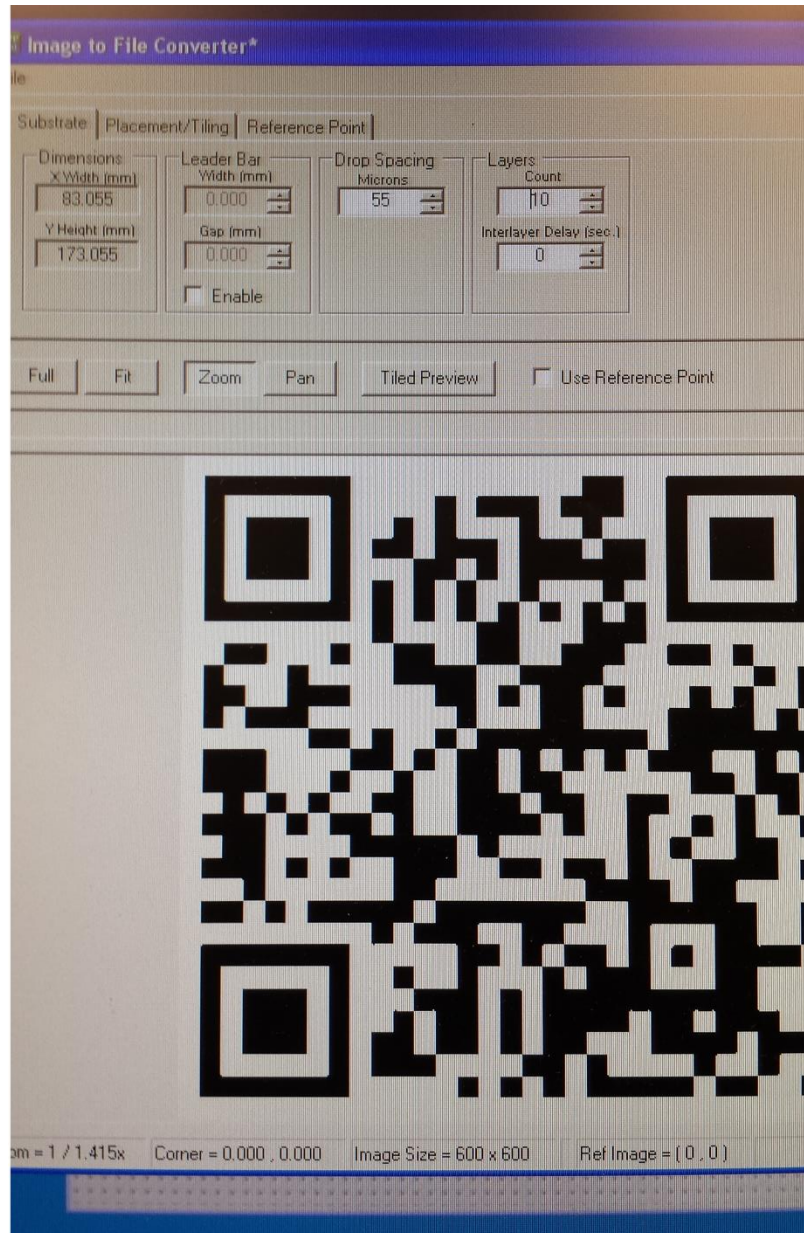
B.2 Waveform Parameters

B.3 Printing Plate Parameters

B.4 Voltage Parameters

B.5 Cartridge Parameters
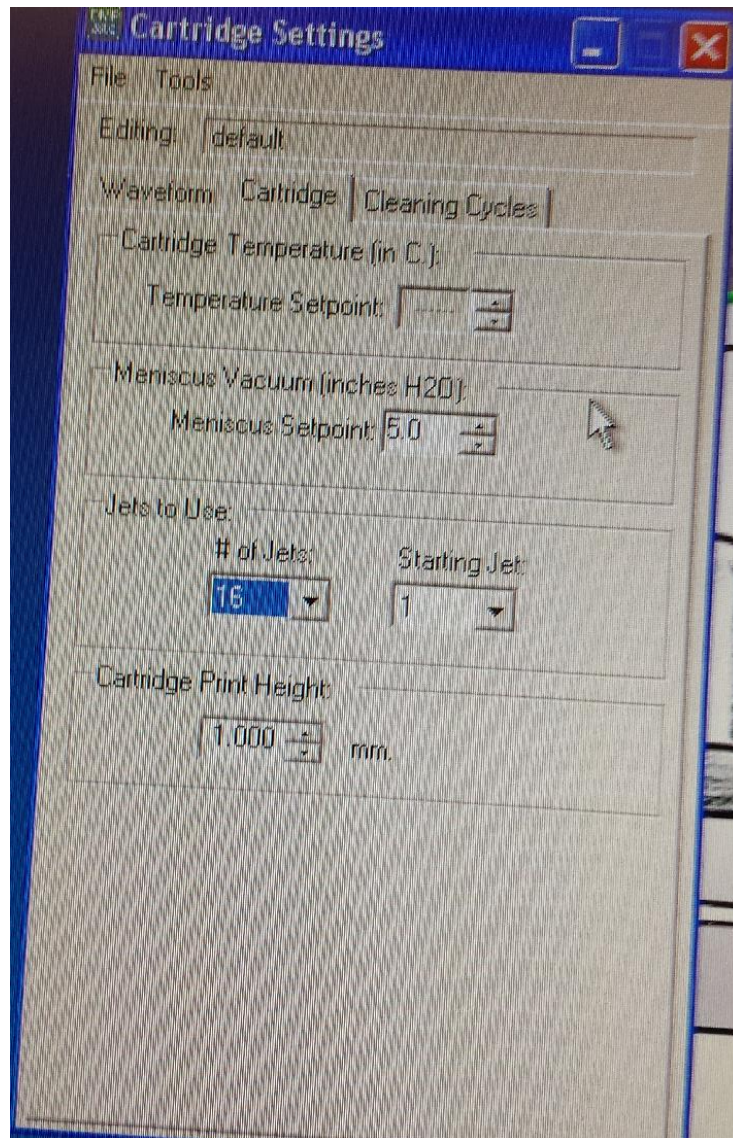
B.6 Cleaning Cycle Parameters

Cartridge Settings

File   Tools

Editing: default

Waveform | Cartridge | Cleaning Cycles |

Start of Printing:
0.5 Spit 0.5 Purge 0.5 Spit   [Select] [Edit]

During Printing:
0.5 Spit 0.5 Purge 0.5 Spit   [Select] [Edit]
Run every:
   10   bands OR   300.0   seconds

End of Printing:
None   [Select] [Edit]

While Idle:
None   [Select] [Edit]
Run every:
1000.0   seconds
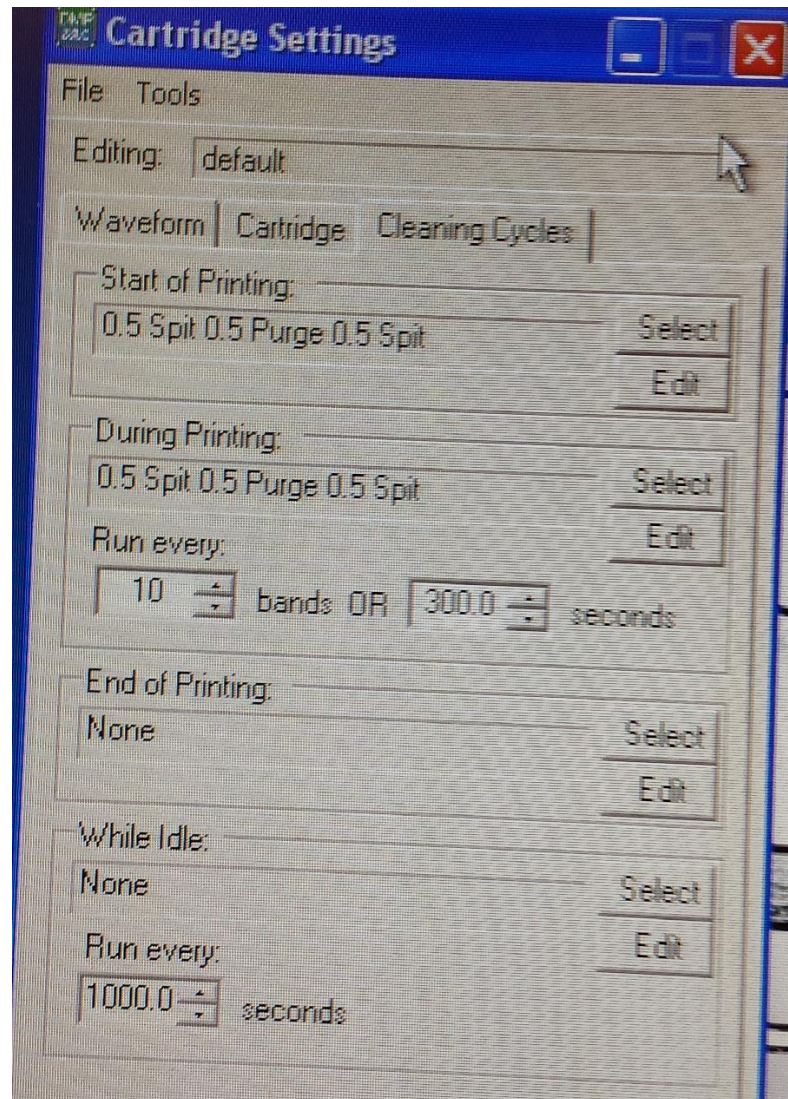
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