UNDERGRADUATE RESEARCH EXPERIENCES REPORTS ON ACNE TREATMENT, HEAVY METAL IN WATER, AND MEASUREMENT OF THE HEAT REACTION OF ISOSORBIDE METHACRYLATE

THOMAS F. FREEMAN HONORS COLLEGE

SENIOR THESIS

BY

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COLLEGE OF SCIENCE, ENGINNERING, AND TECHNOLOGY

MAY 2019

APPROVED BY

HONORS FACULTY FELLOW MENTOR — DATE 04/18/2019

DEAN, HONORS COLLEGE — DATE 4/18/19

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ABSTRACT

UNDERGRADUATE RESEARCH EXPERIENCES REPORTS ON ACNE TREATMENT, HEAVY METAL IN WATER, AND MEASUREMENT OF THE HEAT REACTION OF ISOSORBIDE METHACRYLATE

By

JAIDA LEWIS, B.S.

Texas Southern University, 2019

Dr. Hector C. Miranda, Advisor

This thesis reports on three significant science projects I have done during my undergraduate years. The first part is on the effect of Benzoyl Peroxide and Salicylic, two active ingredients in face wash for acne control, on MCF-7, epithelial cells. My assays suggested that salicylic acid lowered the viability of the MCF-7 cells, meaning it is more likely to decrease the viability of acne cells, while benzoyl peroxide did not seem to have any effect at all, meaning it is safer to use on the skin. My second research involved measurement of heavy metals, such as aluminum, nickel, cadmium, lead, and chromium in commercial drinking water. Heavy metals are in each bottle of water someone drinks and the long term effects go unnoticed because the percentage is so small. The final research involved Isosorbide Methacrylate (IM). The heat of the reaction for Isosorbide Methacrylate is about 40 kJ/mol, for Isobornyl Acrylate (IBOA) the heat of reaction is about 80 kJ/mol, for IA it is about 65 kJ/mol and BPAM had a heat of reaction from 50 kJ/mol to 79 kJ/mol. Mixtures of IM and IBOA had higher heats of reaction than IM and a lower heat of reaction than IBOA.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

VITA

Born	November 4, 1996	Born in Chicago, Illinois
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ACKNOWLEDGEMENT

I would like to give my sincere appreciation to Dr. Hector Miranda for providing me with the knowledge and tools that assisted me with my research. It has been an honor working with you throughout the semester. Another big thank you to Dr. Anita White for encouraging me to do research on something that impacts my life so much such as acne. Your support and hard work was greatly appreciated. I would like to also thank my mentor, Dr. John LaScala at the US Army Research Laboratory for helping me throughout the summer on researching Isosorbide Methacrylate and completing my project. The knowledge that you have provided for me during my studies was greatly appreciated. Last but not least, I would like to thank my family and friends who supported, encouraged and prayed for me during my studies.

INTRODUCTION

Research has been a major part of my life since I attended high school at the Illinois Mathematics and Science Academy, located in Aurora, Illinois. I found love for research on broad chemistry topics that interest me which led to choosing chemistry as my major in college.

This thesis is a compilation of three major experiments that I have done in my four years of college involving industrial products, and environmental samples. The first one is on the effects of two common compounds found in acne medicine, benzoyl peroxide and salicylic acid. Some people really do not understand the effects acne has on how people perceive themselves. Therefore, during the second semester of my junior year of college, I chose to research acne and discuss how it effects society.

Will this acne epidemic ever go away? Many young adults manage the issue of acne daily. It can become a challenging situation when dealing with self-image and self-worth. Numerous commercials are viewed on television with the hope of a miracle cure. Store aisles are inundated with various products as young adults eagerly test them out, one by one, expecting their face will clear from the acne. I personally, have experienced acne issues recently and it has been very difficult to discover what the cause is. Dermatologists have prescribed to me a temporary fix, but still no cure. For example, the face soap, moisturizer, or any other topical creams one uses on their face could be the cause. Another cause of acne is diet. Certain concentrations of glands on the face, or Acne problem can also be hereditary. Acne may also be a genetic problem caused by hormones. If both parents have acne, three out of four children could be affected (Fulton Jr. 95). There are acne-focused groups in the dermatology community such as the American Acne and Rosacea Society and the Global Alliance to Improve Outcomes in Acne (Leyden 2017). Two compounds that are commonly found in acne cream are benzoyl

peroxide. And salicylic acid. However, their effects on skin cell have not been fully explored. I discussed these issues in Chapter 1 and also presented the results of my experiments.

The second chapter of my thesis is on the analysis of the heavy metals chemistry commercial bottled water where I had the opportunity to use sophisticated technology such as the inductively coupled plasma mass spectrometry (ICP-MS) which is extremely sensitive in detecting trace amounts of heavy metals and other elements. Heavy metal pollution is serious problem in many industrialized countries like the United States because at certain and specific levels, they are harmful, and their long term effects range from neurotoxicity to cancer. The most common heavy metals in water include aluminum, nickel, cadmium, lead, chromium, and arsenic.

The third chapter of my thesis is about additive manufacturing and methacrylates. I had the opportunity to research the heat of reaction for methacrylates using Differential Scanning Calorimetry (DSC) and the Fourier-Transform Infrared Spectroscopy (FTIR). Finding this information out will help the United States Army in many ways, especially when they are out in the field. Many of the methacrylates tested had similar characteristics.

CHAPTER 1: EFFECT OF BENZOYL PEROXIDE AND SALICYLIC ACID ON MCF-7 EPITHELIAL CELLS

Acne is a chronic inflammatory disease that involves pathogens of four major factors: androgen-induced increased sebum secretion, altered keratinization, colonization of *Propionibacterium acnes*, and inflammation (Sacchidanand (2017). Sebum is an oily lipid mixture consisting of esters of glycerol, wax, and cholesterol, as well as squalene and fatty acids. Sebum helps lubricate and waterproof the skin and hair and helps block germs from entering the body (Bratsis 2017). Acne is a medical skin condition linked to an unusual sebaceous gland function. The most common acne is referred to as non-inflammatory open or closed comedones and by inflammatory papules, pustules, nodules, and cysts (Engler 2016). Researchers have found some similarities between experiments conducted on people with acne. The results are oily skin will most likely be more susceptible to acne because of oil clogging the pores. Knowing the type of skin that is most susceptible to acne will help people become successful on preventing the acne from occurring on their body. They will be able to buy products which are specifically made for oily skin, in addition to regulating their diet.

The face is usually where acne is the most visible. Sebaceous glands are found all over human skin but it is in greater concentration on the face and scalp (Engler 2016). Researchers, from all the articles investigated, mentioned areas where the most acne occurs is usually the face, upper part of the chest and back. Acne may cause scarring and some hyperpigmentation (Engler 2016). Acne scarring happens as a result of dermal remodeling and an imbalance between matrix

degradation and matrix synthesis (Leyden 2017). Young women and men alike may have developed the habit of popping the pimples they see on their face, thinking this will cause the pimple to go away. In reality, this action only damages the skin and may cause scarring. Many times when the acne is all gone, it still may appear as if it is present on the body due to the spots that remain on the area. It is important that if a person understands this phenomenon, they will learn what not to do to their face or body when acne appears.

In the articles written by Sacchidanand et al. (2017), they all discussed that acne is most common in teenagers and can also persist in adulthood. Around 85% of young people between the ages of twelve to twenty-four have acne and 15-20% of the people have severe problems (Engler 2016). Parents, as well as health teachers, should discuss this crucial time in a person's life when acne may start appearing so it will not be a surprise to teenagers. Hopefully, the young adults will be able to adapt to the changes transpiring on their body. Acne is more common in men during the younger years, but into adulthood, it is more common in women (Engler 2016). During puberty, hormones stimulate the production of sebum, which can clog pores. Bacteria can get trapped in clogged pores and multiply. This causes swelling which is the start of acne. Most teenagers with acne believed this was the most difficult aspect of puberty (Bratsis 2017). When pimples become visible on the face, the cool thing for teenagers is to place Band-Aids on their face to cover up the acne. Since puberty is a new phase in the teenager's life, they have a difficult time treating the acne and determining what products work best for their skin type.

Research, particularly performed by Knaggs 2004, focused on the cessation of acne in adult years, but other researchers have noticed that acne continues throughout the adult years; it

does not stop during the teenage years. A significant and growing body of literature suggests that this disease is becoming more prevalent in adults. Acne is lasting longer and is requiring treatment well into the ages of forty to forty-five. Post-adolescent acne predominately affects women (Knaggs 2004). One controversy is that women tend to receive acne treatments at a higher rate than men, which could be why it seems that post-adolescent acne is more prevalent in women (Knaggs 130). Studies done in the United Kingdom and in Germany show that acne is in fact continuing well into adulthood for both males and females (Knaggs 2004). Some factors that are contributing and could explain post-adolescent acne is the use of cosmetics, stress, resistant bacteria, and oral contraceptives. The sun could even be a factor contributing to acne because of ultraviolet rays (Knaggs 2004). Also, for someone being in the sun often, sunscreen is used and the ingredients in the sunscreen could clog pores if it is not washed off properly after the activities in the sun are complete. Knowledge acquired during teenage years will be helpful when dealing with adult onset acne.

The two major goals of acne therapy are achieving clearance or almost complete clearance of acne lesions and minimizing the potential for long-lasting acne-related scarring, post-inflammatory hyperpigmentation, and erythema (Leyden 2017). Before treatment of acne can occur, assessments need to be performed on the patient's face. Professional analysis is needed to determine the severity of the acne, the skin type, presence of acne scarring, cosmetic products being used, as well as the patient's psychological state (Engler 2016). Acute and chronic stress can both cause different severities of acne. For acute stress, with an aggressive skin care program and removal of all the impactions, the flare-ups will disappear. Chronic stress

is harder to manage. With the increase in hormone levels, more oil is produced which could aggravate the skin (Fulton Jr. 99). People need to realize that what happens throughout their life, whether good or bad, affects their health, how they look, and how they feel. Therefore, in an attempt to avoid acne, one must see professionals, but also try to live life without bad or negative energy.

Mild to moderate and moderate to severe acne are both treated differently. Mild to moderate acne is treated with topical medication whereas moderate to severe acne is treated with oral medication (Engler 2016). These two particular treatments were discussed throughout the experiments and articles read. Retinoids are contained in the tropical medication. They have a potential role in decreasing sebum production and is the preferred choice for scars and post inflammatory hyperpigmentation of the skin (Sacchidanand 342). Knowing how severe one's acne is will determine how the acne should be treated. Topical retinoids have shown both to reduce visible lesions and also inhibit the development of microcomedones and new lesions (Leyden 2017). They also lighten hyper pigmented lesions (Leyden 2017). For oral medication, isotretinoin is an oral retinoid treatment of acne. Isotretinoin targets the four major factors involved (Sacchidanand 349). Oral antibiotics are used for moderate to severe inflammatory acne. They are found to possess antimicrobial as well as anti-inflammatory properties. Either one of these treatments will assist in the disappearance of acne but the amount of time needed for the treatment varies.

How should one treat this nuisance called acne? There are additional ways to treat or prevent acne, other than medicinal, which are becoming more popular. One should conduct

research and speak to their dermatologist before testing these procedures. Chemical peeling is becoming a more common technique in managing acne and acne scars. The most frequently used peeling agents are salicylic acid, glycolic acid, pyruvic acid, lactic acid, mandelic acid, Jessner solution, trichloroacetic acid, and phenol (Kontochristopoulos 179). Glycolic acid peels have been beneficial for rapid improvement on acne patients between the ages of thirteen to forty (Knaggs 135). The chemical peeling exfoliates the skin and removes superficial lesions, followed by regeneration of new epidermal and dermal tissues. The right chemical peel for someone is chosen based on the patient's skin type, acne activity, and the type of scarring. A series of chemical peels could have significant improvement over a short amount of time (Kontochristopoulos 179). During my research, I discovered this acne treatment was not heavily discussed. Chemical peeling treatments bring much controversy. One would have to apply chemicals to the skin when ultimately they want healthy skin. However, is skin really healthy when chemicals have been applied to it? Zinc can be also used for treatment of acne due to its sebosuppressive activity as well as omega fatty acids because it has anti-inflammatory and antioxidant effects (Sacchidanand 352).

Some people are even worried that nutrition may effect acne, but many researchers are not too sure that nutrition and acne are related. There is limited research on this topic, but more studies are underway. One reason there is limited research is because it is costly (Fiedler 7). Many of the food options do not affect acne. Acne is genetic; therefore, what you eat does not make a lot of difference (Fulton Jr. 98). However, researching this topic further could also be

helpful. There may be foods that assist with preventing or treating acne in addition to determining what foods cause it.

The strongest studies suggest that dietary glycemic load can contribute to acne (Assaedi 473). A diet loaded with dairy products can play a crucial role in the development of acne. It may also correlate to the longer duration of acne being present due to the glycemic amount in these products (Sacchidanand 352). Particularly, skim milk presented a significant association with acne as a result of its increased processing and declined estrogen content, compared to whole milk (Assaedi 473). Certainly milk is not the only dietary contributor to acne, but it does give researchers a starting point to determine what other types of foods can effect acne.

Although acne was earlier considered to be a cosmetic affliction, the psychological effects of the disease have now been scientifically proven (Neirita 515). More and more research, whether medication or diet, is being performed on people with acne to determine ways of treating and preventing the disease. Since acne follows a chronic relapsing and remitting course, it is important to have topical medications that decrease the formation of new lesions by targeting the precursor of acne lesions (Leyden 300). The acne epidemic should become more important in society and should be further studied because it is very common amongst males and females, at any age. Acne can have an effect on a person's psychological mindset. "Teenagers with acne reported lower self-confidence or shyness, difficulty finding dates, problems making friends and challenges with school (Bratsis 17)." If these occurring problems begin to decrease, then it could have a positive impact on society. Much research attempts to discover the bases of acne's origin. For prevention, I believe the main focus should be a person's diet and skin type.

The first major project I ever performed was in high school called "The Effect of Benzoyl Peroxide and Salicylic Acid on MCF-7, Epithelial Cells. I chose this topic because acne has always been something with which I struggled. The questions I wanted to answer at the conclusion of that research was, how will the active ingredients in face wash affect skin cells, and how will benzoyl peroxide and salicylic acid affect the viability in MCF-7 cells?

Face wash is a very popular cosmetic item for both men and women. Some use it just for cleansing purposes and others use it specifically to get rid of their acne. Acne, the most common skin disease, is caused by a process in the sebaceous follicle (Kittredge et al, 2008). Benzoyl peroxide and salicylic acid are the most common active ingredients in face wash. Active ingredients are the substances that are supposed to decrease the viability of the acne cells. Because of this, my partner and I tested the effects of these two ingredients on MCF-7 cells. We used MCF-7 cells because of their ability to replicate so quickly. They are breast cancer epithelial cells that duplicate within 36 hours. Our cells were grown in a complete Roswell Park Memorial Institute (RPMI) medium and kept in an incubator because they grow best at 37^{o} Celsius in 5% CO_2 (American Type Culture Collection, 2012).

Epithelial cells can be found lining the cavities of the body. They are the most prolific cells in the body and epithelia tissue is able to act as sensory receptors in the body as well. They are the first cells to be attacked by viruses and create a barrier between the inside and outside of our bodies (ASU). They aid with organ development, tissue regeneration, embryogenesis, tumor progression and fibrosis (Kimura et al, 2013). They have a vascular niche very similar to cancer

stem cells because of their roles during and after metastasis. The cells also have the ability to recapitulate polarity in the tissue by means of in vitro (Lesko et al, 2015).

Benzoyl peroxide has been used for over 45 years and has been shown to be an effective active ingredient in face wash (Baumann, 2014). It has also shown signs of causing skin irritation because of its ability to generate reactive oxygen species (Baumann, 2014). Acne has been shown to improve quickly when treated with benzoyl peroxide (Baumann, 2014). Although it has been shown to cause dry skin, it has also been shown to decrease irritation which allows it to still be effective in some washes (Baumann, 2014). Benzoyl peroxide may also induce toxicity in the cell (Valacchi, 2001). The active ingredient has been shown to congregate in the cell membrane and interact with Vitamin E (Valacchi, 2001).

Salicylic acid has been shown to lower MCF-7 cell viability by inhibiting glycolysis (Spitz et al, 2008). Inhibiting glycolysis does not allow the cell to metabolize and create energy. Without the needed energy, the cells could no longer proliferate or live at all in the acid. Davies and Marks (1976) found that skin treated with salicylic acid had a thinner stratum corneum than untreated skin. Stratum corneum is the most outer layer of the epidermis and since it was thinner after being treated, the salicylic acid was definitely killing the skin cells. Changes were much more obvious with the 6%, 10% and 12% concentrations, but salicylic acid did not have any irritating effect on the skin (Davies & Marks, 1976). It is also an anti-inflammatory drug that induces cellular apoptosis (Spitz et al, 2008).

Active ingredients are usually at about 2% concentration in face washes. The various concentrations were tested 1%, 2.5%, 5%, 7.5% and 10% to see if the percentage would have an

effect on the viability as well. The cells were exposed to the active ingredients for only up to 30 minutes as anything longer would be less relevant to the time that people use these products to wash their faces. Researchers have found that both salicylic acid and benzoyl peroxide affect the cells in some way at all concentrations but there was no significant difference in the effects.

In order to test the viability, an MTT Assay was used. The assay is conducted by putting the plate into a reader that flashed light through the 96-well plate and gave us the absorption. If cells are viable, they will allow light to pass through. If the cells are no longer viable they will absorb the light and therefore have a higher absorbance reading than the other wells. We used a control to compare our results. If the absorbance rate was higher than the control we knew the dilutions had some sort of effect on the cells. Before putting the plate into the reader, dimethyl sulfoxide must be added in order for the cells to releases the absorbed MTT.

The methods I used for this research was as followed:

Cell Plating and maintenance:

Cells were initially plated into a 75 cm^2 flask in 50 mL of RPMI medium containing glutamine, penicillin-streptomycin and 10% fetal calf serum. Following growth to confluency, the old medium was removed from the flask that the cells were grown in. Then I added 5mL of trypsin and EDTA to the flask with the cells and incubated it for five minutes to loosen the cells from the flask. After emptying the flask I added 10 mL of unsupplemented RPMI and shook it to dislodge the cells. The contents were emptied into a centrifuge tube and shaken for 10 minutes at 1000 rpm. The liquid was emptied from the tube and 10 mL of supplemented RPMI was added

to it. The cells were then plated into a 96 well plate. The first four wells in each column contained 100µl from the centrifuge tube.

Dilutions:

I used a 50:50 mixture of polyethylene-glycol (PEG) and water, along with the benzoyl peroxide and salicylic acid to create the dilutions. For the 10% solution, I used 1 mg of the active ingredient and 9 ml of the water/ PEG. For the 7.5% solution, I used .75 ml of the 10% and .25 ml of water/ PEG. For the 5%, I used .5 ml of the 10% solution and .5 ml of water/ PEG. For the 2.5%, I used .25 ml of the 10% solution and .75 ml of water/ PEG. For the 1%, I used .1 ml of the 10% solution and .9 ml of water/ PEG. I also used the water/ PEG solution for our control group.

Experiment:

I began by removing the old medium from the wells. The cells were then rinsed with 100 microliters of phosphate-buffered saline (PBS) in each well. After being rinsed, we added 200 microliters of the dilutions to the wells. The first column was control, then 1%, 2.5%, 5%, 7.5% and lastly 10%. The next six wells were in the same order but they contained benzoyl peroxide, instead of salicylic acid. The 96 well plates were then incubated for 15 minutes for the first 3 trials and 30 minutes for the last 2. The solution was then removed from each well and they were rinsed with 200 microliters of PBS again. I then added 150 microliters of RPMI and 50 microliters of MTT Assay to each well. The plates were then incubated for three hours. After the three hours, the solution was removed from each well. The wells were again rinsed with 200

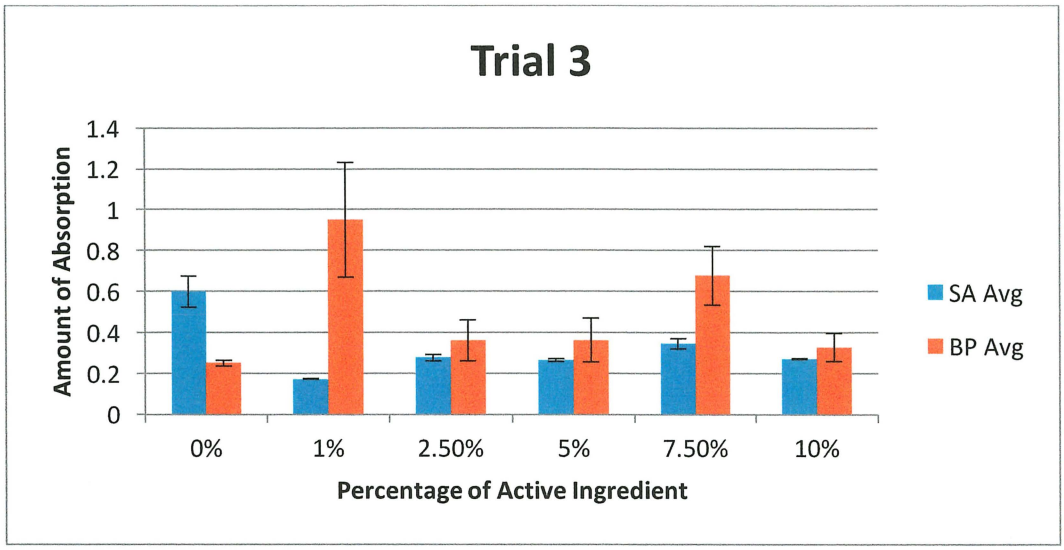

Figure 3: This is the data from a 15 minute incubation. It shows the difference in averages and the error bars show the standard deviation.

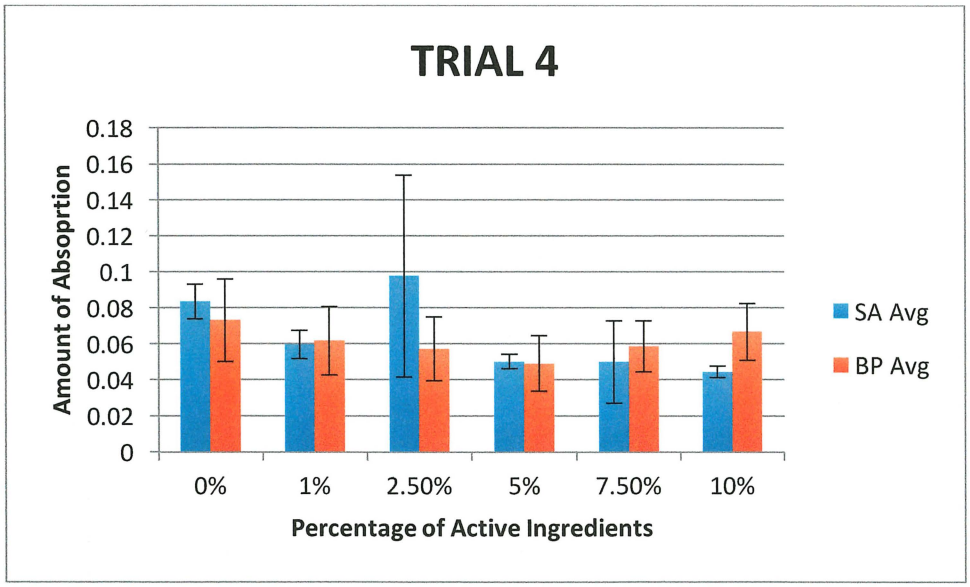

Figure 4: This is the data from a 30 minute incubation. It shows the difference in averages and the error bars show the standard deviation.

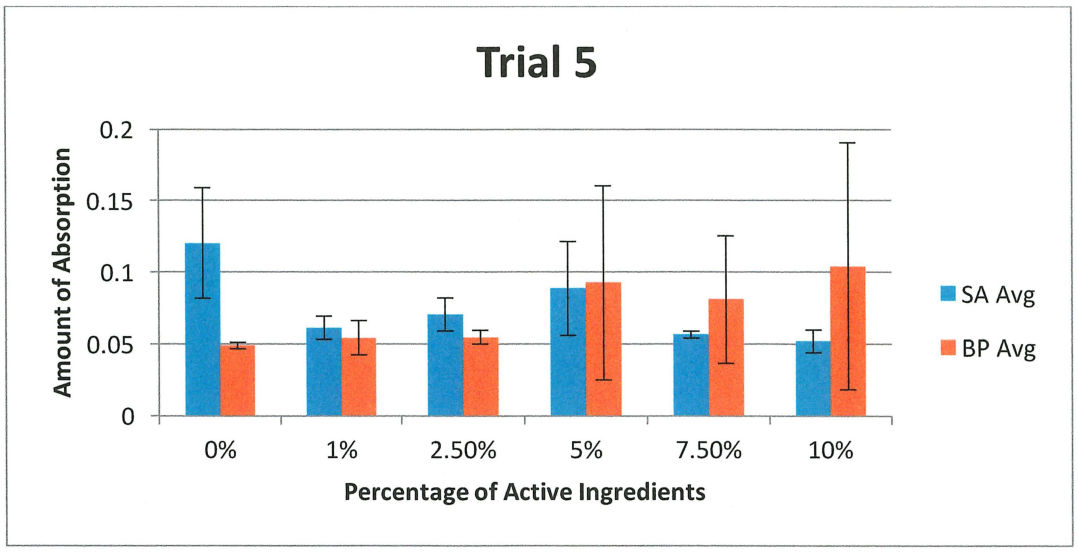

Figure 5: This is the data from a 30 minute incubation. It shows the difference in averages and the error bars show the standard deviation.

Figure 1 shows that salicylic acid has an effect on the cells for all concentrations but the benzoyl peroxide did not have an effect until 7.5%. Figure 2 disproved the results from Figure 1 showing that salicylic acid had no effect, while benzoyl peroxide did, which led us to perform another trial. Figure 3 again shows that salicylic acid has an effect at all concentrations and benzoyl peroxide did not. After allowing the cells to be incubated for 30 minutes, as shown in figures 4 and 5, salicylic acid affected the cells at every concentration, but benzoyl peroxide still did not have an affect. The large standard deviation bars could be due to the different number of cells in each well or because I made our own 96-well plates for the experiment. I have become more of a hands on learner because of this. I was able to plate cells myself after watching one or two times and running experiments by myself after creating my own procedure.

Salicylic acid lowered the viability of the MCF-7 cells, meaning it is more likely to decrease the viability of acne cells. In conclusion, salicylic acid is the better active ingredient to

look for in face wash based off of the results. If you are looking for a less potent face wash, benzoyl peroxide is the ingredient to look for. I also noticed that the concentration did not make a difference in how each one affected the cells. Face wash usually has a 2% concentration and we tested from 1% to 10%, each one having the same effect as the others.

Because of my results, I know that salicylic is more effective for killing acne cells. There were less viable cells in the wells with the active ingredient added. Benzoyl peroxide did not seem to have any effect at all, and thus safer to use on the skin. Some of the error bars are extremely large on the graphs, informing us that our data is not the most accurate. The large standard deviations could also be due to the different number of cells in each well.

After this research, I looked more closely at the products that I used on my skin. I tried to go for products that had less salicylic acid and more benzoyl peroxide so that it would not cause as much harm to my skin. I learned that my skin worked best with gentler products and harsher products cause my skin to break out even more. I was able to find the best products for my face and ever since then my face has been clearing up and continues to get better as the days go on, but it is still a work in progress. I wonder if there could be other chemicals that have even better effects than salicylic acid and benzoyl peroxide.

CHAPTER 2: HEAVEY METALS IN SIX COMMERCIAL WATER BOTTLES

In my junior year, I conducted research on heavy metals in six different bottled waters. Coastal ecosystems are very important for everyday society and living. Many animals live in the coastal ecosystems or feed off of the animals living there. When natural disturbances occur, such as hurricanes, it can cause physical and ecological changes. The changes could be in organic matter, nutrients, or even salinity. All of these changes may affect the primary producer and consumer community composition. Storm events and a lot of heavy rainfall can produce contaminants in raw water. Surface water supplies some communities with drinking water, but it can contain many contaminants such as heavy metals. Heavy metal pollution is a major problem that affects the aquatic ecosystem. Its removal from polluted water depends on the type of metal ions, agricultural wastes and the contact time at which the water was tested. Intense activity in industrial and agricultural sectors has led to an increase in the levels of heavy metals in natural water. Access to safe drinking water has become a huge challenge to regulators and require screenings of potentially hazardous chemicals especially when there are investigations on water quality. Having these toxins in the water could be associated to common illnesses that people could receive.

Large amounts of heavy metals can have harmful effects on human health. Contaminants existing in drinking water can be released into the bloodstream through the digestive tract. Therefore, when analyzing drinking water, it is important to look at the elements such as aluminum, nickel, cadmium, lead, and chromium. A high level of nickel can cause nickel

toxicity and increased aluminum can cause acute toxicity which could lead to brain and bone diseases through the disturbed balance of calcium phosphate. The World Health Organization designated arsenic, cadmium, and lead to be some of the heavy metals that are harmful to human health. The maximum concentration of these metals in drinking water for arsenic is 0.01mg/L, for cadmium 0.003mg/L and for lead 0.01mg/L. Because of the increase of environmental pollution, treatment and the removal of the heavy metals from water has become much harder. Chemical precipitation is the most common treatment to remove heavy metals, but has become more difficult because of the large amounts of sludge that come from the environmental water sources.

By using inductively coupled plasma mass spectrometry (ICP-MS), there can be an accurate determination of heavy metals in geological materials such as soil and water. ICP-MS is the most sophisticated and reliable technique for determining and quantifying trace metals. It has advantages of high sensitivity, low detection limit and fast analysis speed, while determining a variety of elements simultaneously.

The methods used for this project are as follows:

Preparing Samples:

50mL of each water sample (Nice, Smartwater, Fiji, Ice Canyon, Evian, and Iceland) was poured into 6 vials. Then 2.86 mL was extracted from each vial in order to add 1.43mL of Nitric Acid and 1.43mL of Hydrochloric Acid so the total amount was still 50mL. I mixed each vial well. Then poured 10 mL of each into smaller vials in order to perform the ICPMS.

General ICPMS Procedure for Bottled Water: https://www.perkinelmer.com/lab-solutions/resources/docs/APP_NexION300D-US-EPA200-8-Drinking-Water.pdf

Ignite plasma, allow 30 minutes to warm up. Optimize instrument, as per instrument manufacturer's instructions. Perform mass calibration check – adjust if change is > 0.1 amu. Perform resolution check – adjust if > 0.75 amu at 5% peak height. Calibrate using blank and standards. Monitor all masses necessary for interference correction. Screen new samples for relative levels and presence of internal standards. Run instrument performance evaluation tests:

– Instrument detection limits (IDLs)

– Method detection limits (MDLs)

– Linear dynamic range (LDR)

– Spike recoveries

– Long-term stability

Run quality control samples (QCSs) or standard reference materials (SRMs) such as: High-Purity Standards Trace Metals in Drinking Water (TMDW), both neat and diluted. Run unknown samples (e.g. local tap water). Review results of quality control samples for pass/fail criteria.

Below are the graphs and the results of the ICPMS test as well as how the amount of nitric acid and hydrochloric acid was calculated.

Nitric Acid:

$$70M \times V1 = 2M \times 50mL$$

V1=1.43mL

Hydrochloric Acid:

$35M \times V1 = 1M \times 50mL$ V1=1.43mL

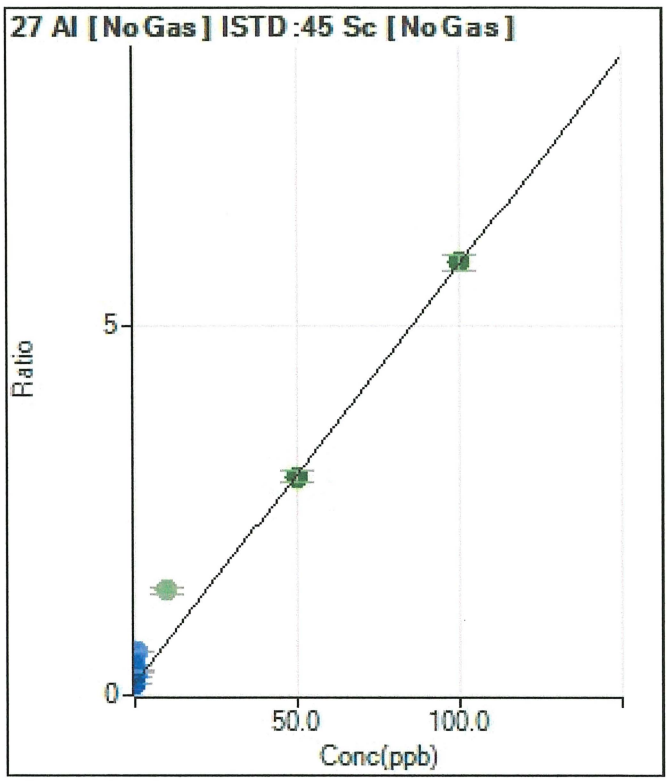

Figure 6: The concentration of aluminum verses the volume tested

	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.014	151888.69	0.1578	P	1.2
2	☑	0.050		269700.83	0.2497	P	2.0
3	☑	0.100		428109.38	0.4057	P	5.5
4	☑	0.500		344788.65	0.3245	P	2.3
5	☑	1.000		649074.78	0.5935	P	1.6
6	☑	10.000		1514923.27	1.4177	A	5.4
7	☐	50.000	49.472	3132675.64	2.9585	A	4.6
8	☐	100.000	100.522	6144410.59	5.8495	A	3.6

$y = 0.056630 * x + 0.156962$

$R = 1.0000$ $DL = 0.1018$ $BEC = 2.772$

Table 1: The data points for the concentration of aluminum

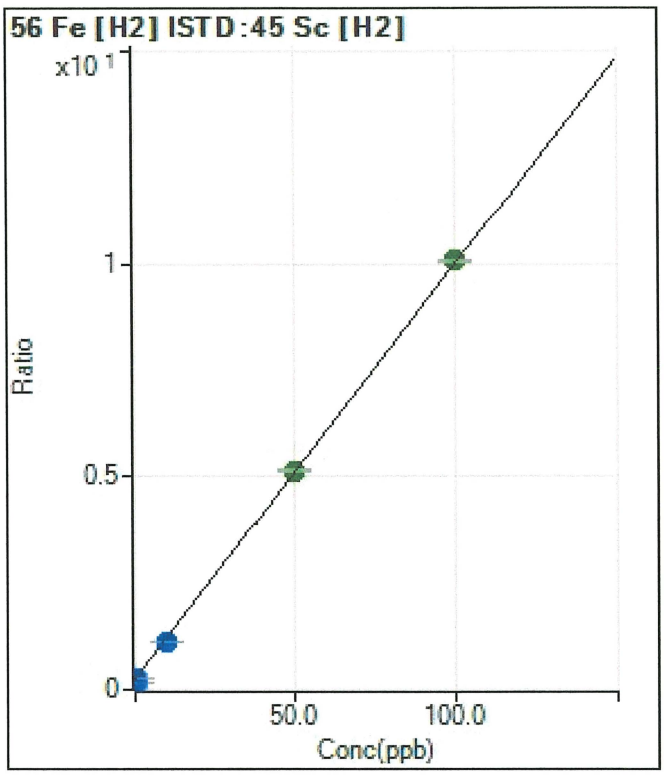

Figure 7: The concentration of iron verses the volume tested with hydrogen as a reference

	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.266	148548.32	0.2794	P	1.5
2	☑	0.050		72723.01	0.1376	P	1.4
3	☑	0.100		85754.08	0.1603	P	1.1
4	☑	0.500		90540.11	0.1716	P	1.3
5	☑	1.000		145697.47	0.2754	P	0.9
6	☐	10.000	8.805	591088.03	1.1112	P	0.8
7	☐	50.000	50.155	2691474.41	5.1395	A	0.9
8	☐	100.000	100.932	5247980.90	10.0862	A	0.6

$y = 0.097419 * x + 0.253451$

$R = 0.9999$ $DL = 0.1299$ $BEC = 2.602$

Table 2: The data points for the concentration of iron with reference to hydrogen

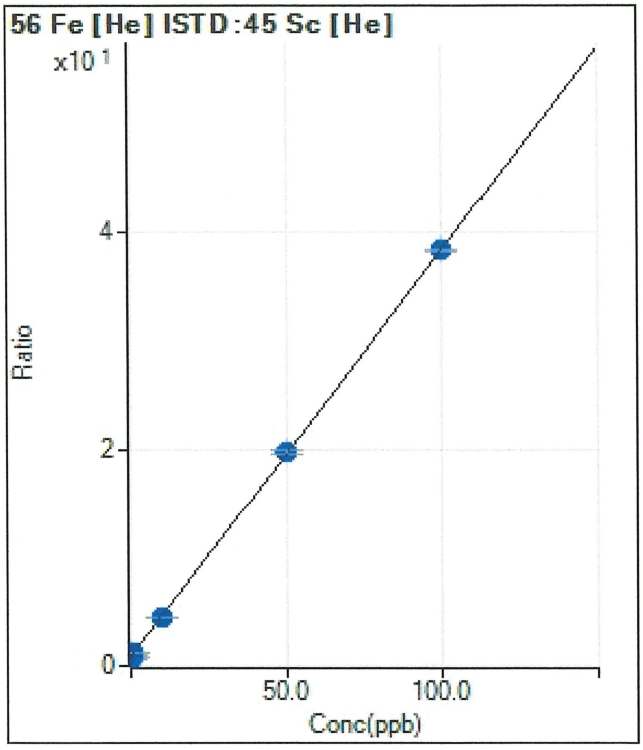

Figure 8: The concentration of iron verses the volume tested in reference to helium

	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.359	17943.60	1.0291	P	6.3
2	☑	0.050		10916.44	0.5695	P	1.4
3	☑	0.100		13569.85	0.6546	P	2.3
4	☑	0.500		15190.38	0.7302	P	1.8
5	☐	1.000	0.675	24714.68	1.1471	P	0.9
6	☐	10.000	9.616	95733.30	4.4940	P	1.0
7	☐	50.000	50.347	409575.53	19.7402	P	1.5
8	☐	100.000	100.099	812063.07	38.3629	P	0.8

$y = 0.374311 * x + 0.894648$

$R = 1.0000$ $DL = 0.5191$ $BEC = 2.39$

Table 3: The data points for the concentration of iron in reference to helium

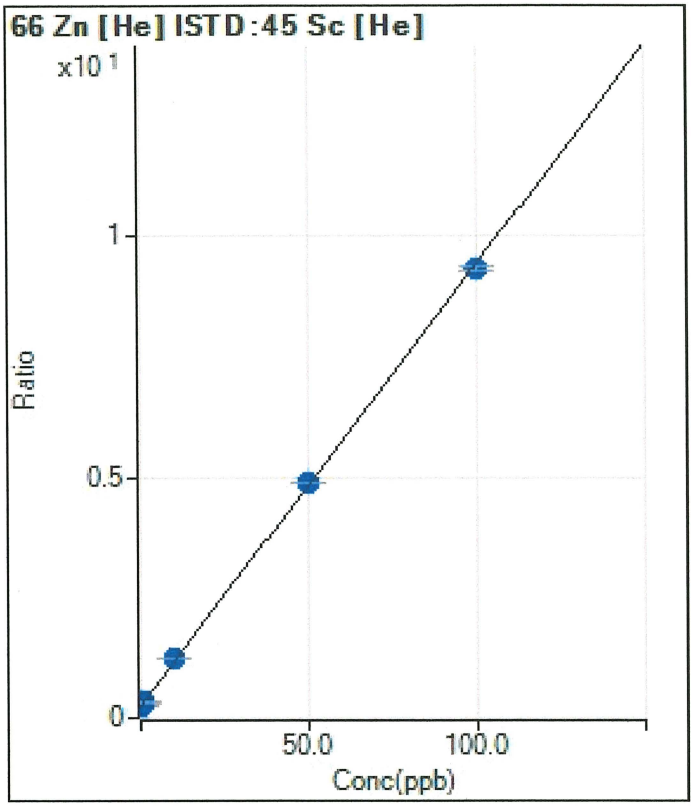

Figure 9: The concentration of zinc verses the volume tested

	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.125	4502.98	0.2577	P	4.3
2	☑	0.050		5423.32	0.2830	P	1.8
3	☑	0.100		7207.45	0.3476	P	1.5
4	☐	0.500	0.321	5734.55	0.2757	P	2.4
5	☐	1.000	0.822	6925.09	0.3215	P	1.8
6	☐	10.000	10.894	26499.11	1.2440	P	1.3
7	☐	50.000	50.621	101305.61	4.8824	P	0.5
8	☐	100.000	98.823	196796.45	9.2970	P	0.9

$y = 0.091586 * x + 0.246246$

$R = 0.9999$ $DL = 0.3647$ $BEC = 2.689$

Table 4: The data points for the concentration of zinc

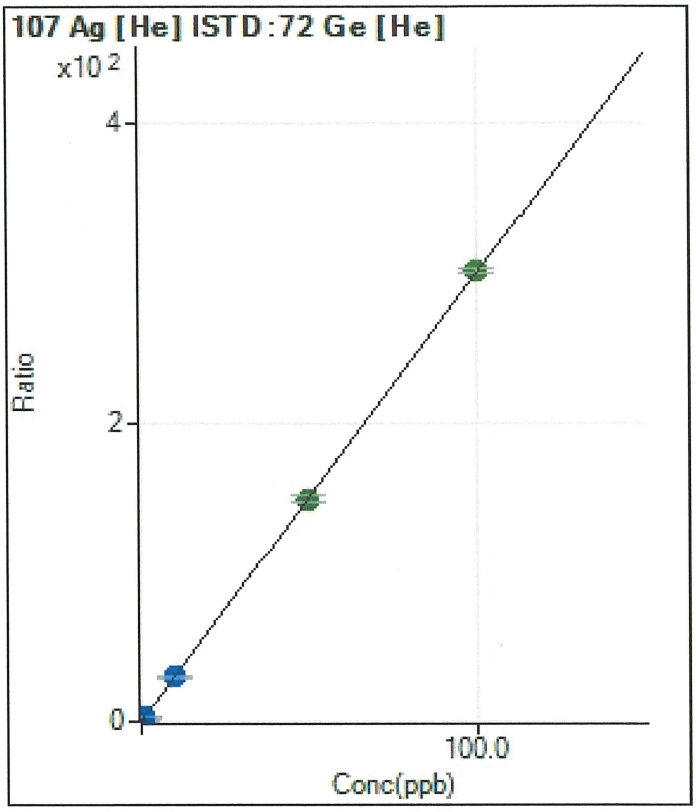

Figure 10: The concentration of silver verses the volume tested

	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.007	702.25	0.1039	P	6.9
2	☐	0.050	0.044	1590.11	0.2156	P	7.3
3	☐	0.100	0.093	2904.78	0.3613	P	3.8
4	☐	0.500	0.489	12671.44	1.5465	P	1.3
5	☐	1.000	0.970	25126.15	2.9885	P	1.4
6	☐	10.000	9.856	243225.00	29.5959	P	1.3
7	☐	50.000	49.642	1221495.51	148.7376	A	3.0
8	☐	100.000	100.559	2478451.50	301.2097	A	1.1

$y = 2.994517 * x + 0.082713$

$R = 1.0000$ $DL = 0.007195$ $BEC = 0.02762$

Table 5: The data points for the concentration of silver

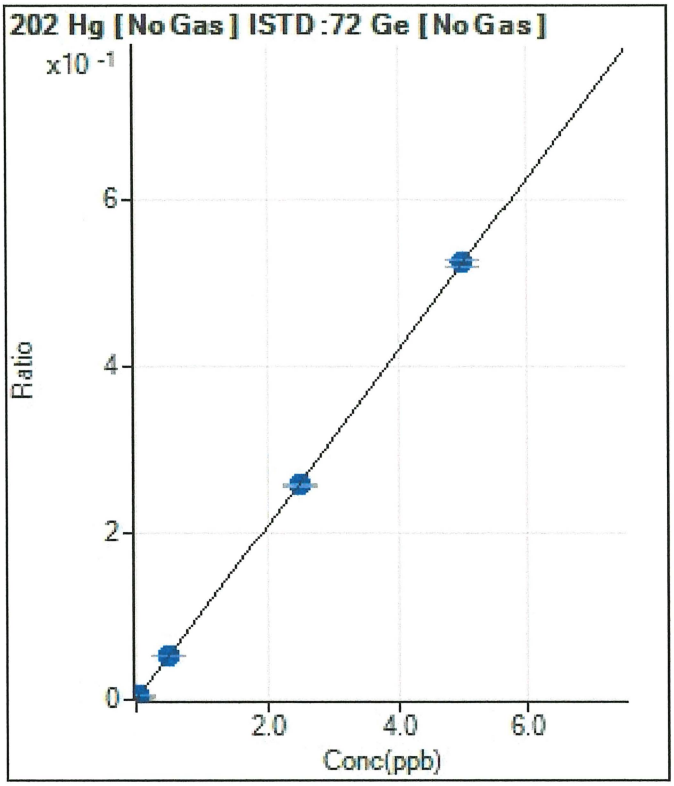

Figure 11: The concentration of mercury verses the volume tested

	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.000	39.33	0.0003	P	8.4
2	☑	0.003		74.67	0.0006	P	13.4
3	☐	0.005	0.005	105.00	0.0008	P	5.1
4	☐	0.025	0.028	420.01	0.0033	P	3.2
5	☐	0.050	0.056	792.69	0.0062	P	7.1
6	☐	0.500	0.506	6784.11	0.0530	P	0.9
7	☐	2.500	2.463	32910.11	0.2568	P	1.5
8	☐	5.000	5.024	66673.57	0.5235	P	1.8

$y = 0.104126 * x + 3.560886E-004$

$R = 1.0000$ $DL = 0.0007441$ $BEC = 0.00342$

Table 6: The data points for the concentration of mercury

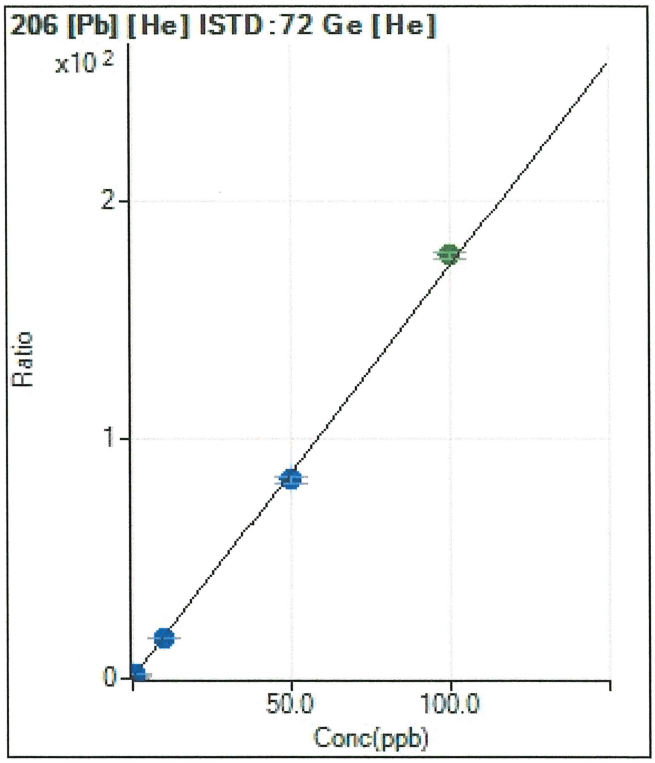

Figure 12: The concentration of lead verses the volume tested

	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.173	4715.36	0.6966	P	5.0
2	☑	0.050		1554.56	0.2106	P	4.4
3	☑	0.100		2383.58	0.2965	P	2.5
4	☐	0.500	0.369	8475.07	1.0345	P	1.3
5	☐	1.000	0.830	15343.58	1.8249	P	0.9
6	☐	10.000	9.656	139593.78	16.9868	P	1.9
7	☐	50.000	48.064	681288.27	82.9656	P	3.3
8	☐	100.000	102.699	1454910.12	176.8206	A	1.4

$y = 1.717847 * x + 0.399871$

$R = 0.9995$ $DL = 0.06022$ $BEC = 0.2328$

Table 7: The data points for the concentration of lead

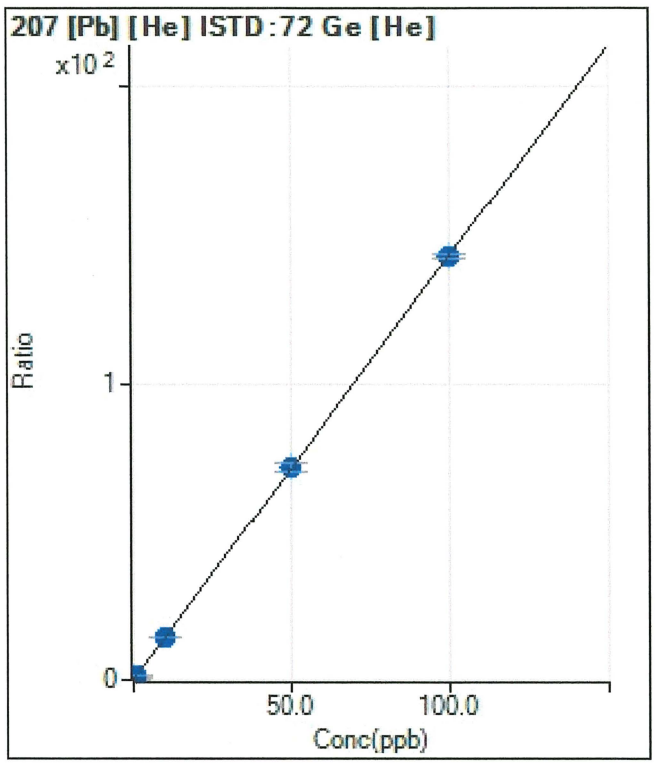

Figure 13: The concentration of lead verses the volume tested at another isotope

	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.299	4151.82	0.6139	P	5.8
2	☐	0.050	-0.001	1375.65	0.1857	P	9.1
3	☐	0.100	0.052	2101.30	0.2615	P	7.2
4	☐	0.500	0.488	7224.30	0.8820	P	4.4
5	☐	1.000	0.968	13171.20	1.5666	P	1.8
6	☐	10.000	10.055	119269.80	14.5132	P	1.6
7	☐	50.000	50.115	587824.04	71.5918	P	3.8
8	☐	100.000	99.917	1172950.58	142.5503	P	1.0

y = 1.424818 * x + 0.187237

R = 1.0000 DL = 0.07503 BEC = 0.1314

Table 8: The data points for the concentration of lead at another isotope

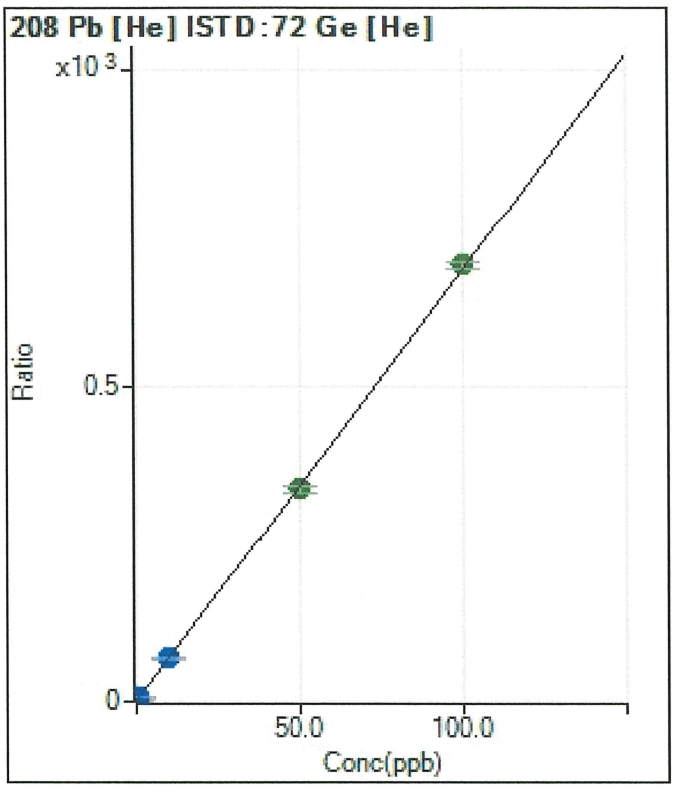

Figure 14: The concentration of lead verses the volume tested at a third isotope

	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.292	19009.01	2.8078	P	3.0
2	☐	0.050	0.006	6306.24	0.8540	P	2.6
3	☐	0.100	0.054	9487.01	1.1800	P	2.8
4	☐	0.500	0.486	33888.82	4.1367	P	2.0
5	☐	1.000	0.956	61776.14	7.3482	P	2.3
6	☐	10.000	9.833	558998.74	68.0207	P	1.5
7	☐	50.000	49.140	2764964.65	336.6832	A	3.0
8	☐	100.000	101.153	5695475.64	692.1911	A	1.3

$y = 6.834971 * x + 0.814329$

$R = 0.9999$ $DL = 0.0371$ $BEC = 0.1191$

Table 9: The data points for the concentration of lead at a third isotope

Nice water has 4.11 ppb of aluminum, no iron using hydrogen, but 0.345 ppb using helium. It has 356 ppb of zinc, 0.0874 ppb of silver, 0.00692 ppb of mercury, and no lead present.

Iceland water has 24.0 ppb of aluminum, no iron using hydrogen, or helium. It has 1.07 ppb of zinc, no silver, 0.00577 ppb of mercury, and no lead present.

Evian water has 4.17 ppb of aluminum, no iron using hydrogen, or helium. It was no zinc, 0.00863 ppb of silver, 0.00288 ppb of mercury, and no lead present.

Smartwater has 12.1 ppb of aluminum, 4.23 ppb of iron using hydrogen, and 4.83 ppb of helium. It has 1028 ppb of zinc, 0.274 ppb of silver, 0.00254 ppb of mercury. For lead, at isotope 206 it was no lead present, but at isotope 207 it was 0.00679 ppb present and at isotope 208, it was 0.0169 ppb present.

Fiji water has 7.25 ppb of aluminum, no iron using hydrogen, or using helium. It has 227 ppb of zinc, 0.0281 ppb of silver, 0.00503 ppb of mercury, and no lead present.

Ice Canyon water has 13.5 ppb of aluminum, no iron using hydrogen, or using helium. It has 2.76 ppb of zinc, no silver, 0.00949 ppb of mercury, and no lead present.

Through this project, I was able to learn just how important the treatments of water are and how so many of the bottled waters are very different from one another. I never realized how many heavy metals could be in each bottle of water someone drinks and the long term effects they could have on the body, but since the percentage is so small, it goes unnoticed. This project forced me to take a second thought about which bottled waters to drink and which ones not to

drink. I wonder if there would be different results from testing spring water verses alkaline water. That could be another project in the future, for me to test.

CHAPTER 3: MEASUREMENT OF THE HEAT OF REACTION OF ISOSORBIDE METHACRYLATE

The summer before my senior year of college I got the wonderful opportunity, through the Thurgood Marshall College Fund, to complete an internship at the U.S. Army Research Laboratory in Aberdeen Proving Ground, Maryland. For my project, I wanted to find the "Measurement of the Heat of Reaction of Isosorbide Methacrylate" and how it will correspond with additive manufacturing which is three dimensional printing.

The purpose of Additive Manufacturing (AM) will allow soldiers to produce three dimensional products at the point of need, increase readiness, improve sustainability, and improve survivability, lethality, etc. The literature says that the heat of reaction is between 12-22 kcal/mol which is equivalent to 50-92 kJ/mol but it varies depending on the R group. It is beneficial to know the heat of reaction of Isosorbide Methacrylate to enable quick determination of the extent of cure, engineering for AM, and engineering for composite fabrication. The cure through Differential Scanning Calorimetry (DSC) is likely to be incomplete so there would be a need to determine the extent of cure through other means. The Fourier-Transform Infrared Spectroscopy (FTIR) can be used to measure the extent of cure.

The advantages of Isosorbide Methacrylate are it eliminates the need for volatile diluents and enables cheaper processing. It also enables the use near engine components, has high

temperature epoxy performance at 1/10th of the cost and has excellent potential for Photocure additive manufacturing.

For this experiment, the questions addressed were the following: 1) what is the heat of reaction of IM methacrylate, 2) does the heat of reaction change with composition, is Isosorbide Methacrylate's (IM) heat of cure significantly different from Bisphenol A Dimethacrylate's (BPAM) heat of cure, and 3) does Isosorbide Acrylate (IA) have a significantly different heat of cure than IM?

Differential Scanning Calorimetry (DSC) was used to first find the heat of reaction in joules per gram. Ideally, a jump and isothermal hold was used, which was the simplest method to replicate with other analytical tools and most analogous to AM and composites processes. A ramp postcure was added to 250 °C to polymerize the material as much as possible. Ramp cures or alternative cure schedules were used if isothermal cures proved troublesome.

For the FTIR Method, the FTIR instrument, heating cell, and temperature controller was used to measure the actual extent of cure. The ramp procedure used matches the DSC method (5 °C /min to 250 °C).

The results of my research are as follows:

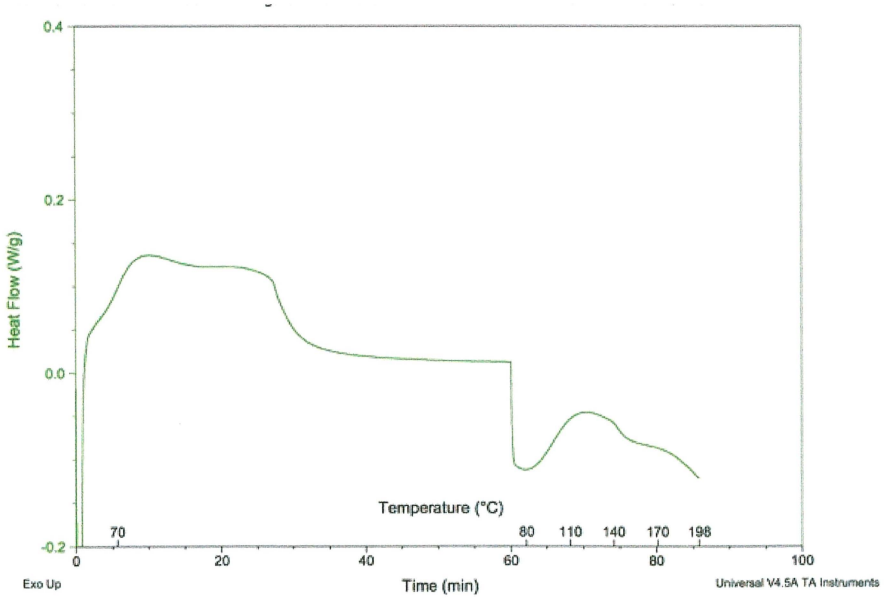

Figure 15: The jump and isothermal method

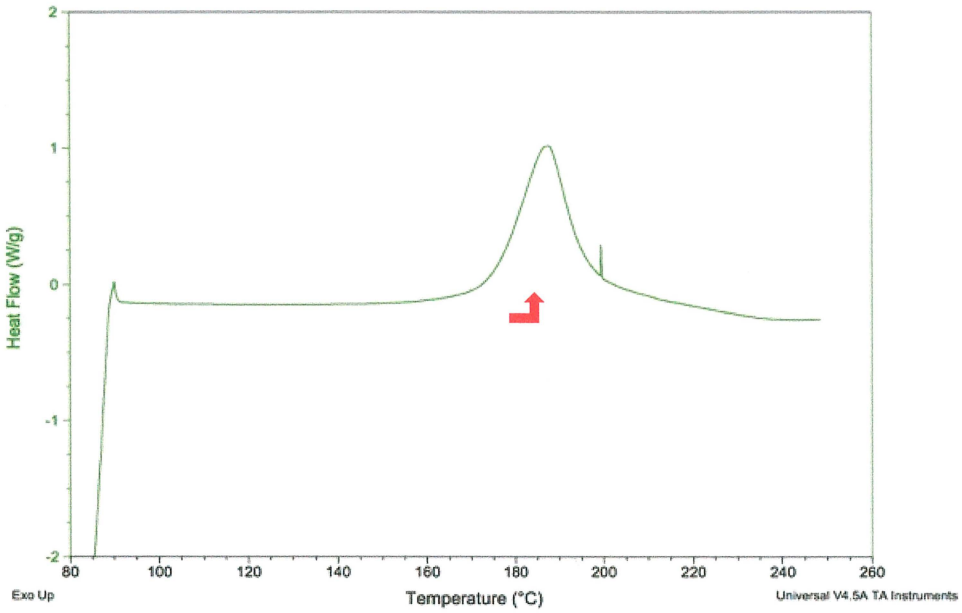

Figure 16: A jump and isothermal method with inhibitor added

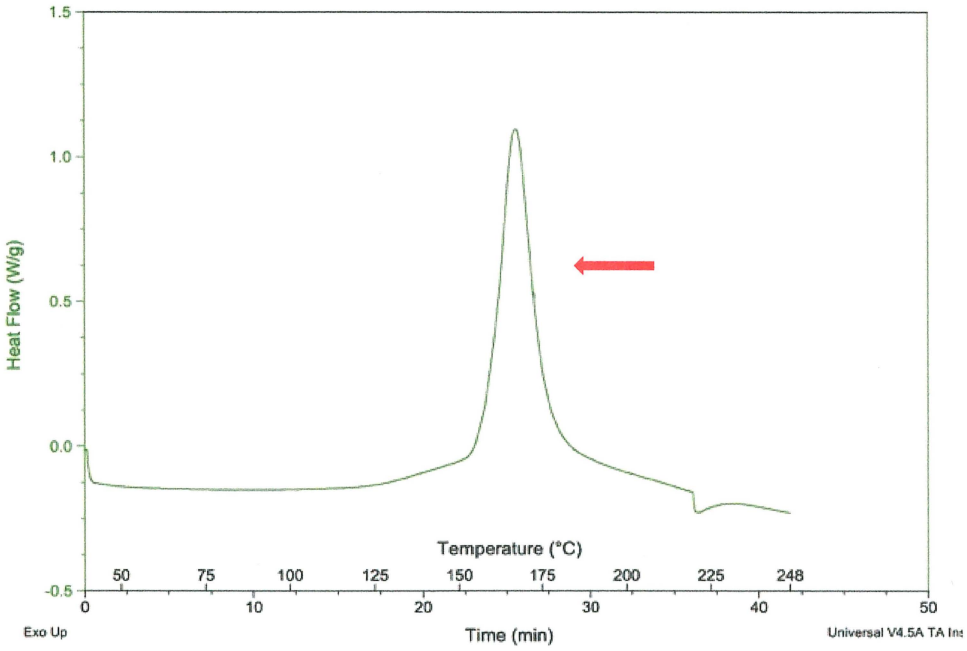

Figure 17: The method of 5 °C per minute at a ramp to 250 °C

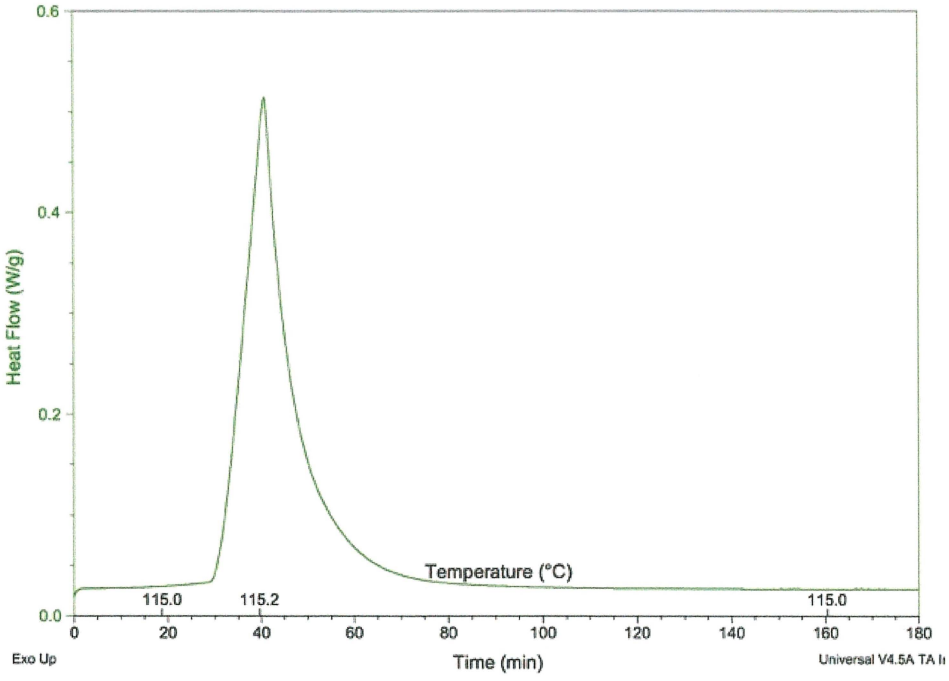

Figure 18: An isothermal procedure

	Heat of Reaction (J/g)
IM	**232.2**
IBOA	**359**
IM + 20%IBOA	**233.1**
IM + 35%IBOA	**285.7**
IM + 50%IBOA	**302.7**
BPAM + 25%IBOA	**247.7**
BPAM + 50%IBOA	**350.9**
IA + 50%IBOA	**408.6**

Table 10: Displays the heat of reaction of all the substances in J/g

	Total Extent of Cure
IM	82%
IBOA	100%
IM + 20%IBOA	81%
IM + 35%IBOA	82%
IM + 50%IBOA	83%
BPAM + 25%IBOA	69%
BPAM + 50%IBOA	97%
IA + 50%IBOA	99%

Table 11: The percentages at which each substance cured are shown

	Heat of Reaction (J/g)	Heat of Rxn (kJ/mol)	Corrected Heat of Rxn (kJ/mol)	Predicted Corrected Heat of Rxn (kJ/mol)
IM	232.2	32.7	39.8	
IBOA	359	74.7	74.7	
IM + 20% IBOA	233.1	35.3	43.7	36.5
IM + 35% IBOA	285.7	45.7	56.1	40.9
IM + 50% IBOA	304.5	51.8	62.5	46.4
BPAM + 25% IBOA	247.7	47.2	67.9	40.5
BPAM + 50% IBOA	350.9	68.3	70.6	55.4
IA + 50% IBOA	408.6	64.4	64.8	

Table 12: The results once the heat of reaction was converted to kJ/mol

Figure 1 is the jump and isothermal method. This did not allow for good quantification of the heat of reaction. The first peak gave a value of 134 J/g and the second peak gave a value of 55 J/g which totaled to 189 J/g, an inaccurate number.

For Figure 2, this is the result of a jump and isothermal method with inhibitor added, which gave a good heat of reaction value of 230 J/g. The process with the inhibitor added took a long time to cure.

In Figure 3, the method of 5 °C per minute at a ramp to 250 °C was evaluated. The heat of reaction found was 232.2 J/g.

Figure 4 was an isothermal procedure. A ramp could not be used on FTIR because IBOA's boiling point is ~120 °C, so it evaporated. The heat of reaction did yield 359 J/g.

Table 1 displays the heat of reaction of all the substances in J/g. The heat of reaction in J/mol could not be determined until the extent of cure was found using the FTIR.

In Table 2, the percentages at which each substance cured are shown. Most samples cured to greater than 80%. The extent of cure increased depending on the amount of IBOA content.

Table 3 represents the results once the heat of reaction was converted to kJ/mol. IM has lowest heat of reaction. IA likely has a similar heat of reaction to IM. BPAM has a higher heat of reaction than IM. The predicted heats of reaction for mixtures is lower than the actual value.

The heat of reaction of Isosorbide Methacrylate is about 40 kJ/mol, 9.56 kcal/mol which was lower than known results of other (meth)acrylates. It was noticed that the heat of reaction

changes with composition but it does not obey the rule of mixtures, likely due to higher heat of polymerization of copolymers. Bisphenol A Dimethacrylate has a heat of reaction that is higher than Isosorbide Methacrylate. Isosorbide Acrylate has a heat of reaction about the same as Isosorbide Methacrylate.

Through this summer internship, I learned how much I enjoy being in the lab. Being able to synthesize the substances I was using and others on my own with just the assistance of my mentors was a great experience. I had to learn to be very strategic when measuring chemicals and handling to make sure I did not contaminate any of the chemicals. I understood the purpose and just how important my lab book was for collecting data and taking notes. It is very necessary in the professional field to stay organized because there are many experiments going on simultaneously and you do not want any confusion. I was also able to learn how to use other laboratory tools and how to interpret the data received.

SUMMARY

My research experiences were quite diverse, but they provided me with a more comprehensive experience in chemistry, especially on environmental toxicology.

My research on benzoyl peroxide and salicylic acid taught me a lot on acne. Because of my results, I know that salicylic is more effective for killing acne cells. There were less viable cells in the wells with the active ingredient added. Benzoyl peroxide did not seem to have any effect at all, and thus safer to use on the skin. I now look more closely at the products that I use on my skin. I try to go for products that have less salicylic acid and more benzoyl peroxide so that it would not cause as much harm to my skin.

Through the project of testing the drinking water, I was able to learn just how important the treatments of water are and how so many of the bottled waters are very different from one another. I never realized how many heavy metals could be in each bottle of water someone drinks and the long term effects they could have on the body, but since the percentage is so small, it goes unnoticed. This project forced me to take a second thought about which bottled waters to drink and which ones not to drink. I wonder if there would be different results from testing spring water verses alkaline water. That could be another project in the future, for me to test.

For my last research, the heat of reaction of Isosorbide Methacrylate is about 40 kJ/mol, 9.56 kcal/mol which was lower than known results of other (meth)acrylates. It was noticed that the heat of reaction changes with composition but it does not obey the rule of mixtures, likely due to higher heat of polymerization of copolymers. Bisphenol A Dimethacrylate has a heat of reaction that is higher than Isosorbide Methacrylate. Isosorbide Acrylate has a heat of reaction about the same as Isosorbide Methacrylate.

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