Hidden Toxins in Everyday Cosmetic

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Hidden Toxins in Everyday Cosmetics

Bard College

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Senior Project Thesis
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At Bard College

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Dedication

This thesis is dedicated to my parents, Philip and Paula Morris, for always believing in me and pushing me to strive for greatness. They have taught me that even when life takes an unexpected turn to always stay strong and things will get better. Thank you.
Acknowledgments

I would first like to thank my advisor, Chris LaFratta, for guiding me through not only senior project but also the challenges we faced along the way. I would also like to thank my basketball coach, Casi Donelan-Dobbins, for coming in my junior year and mentoring me both on and off the court. I owe tribute to my sisters, Brenda and Ashley Morris, who have taught me that hard work and dedication will pay off in the long run. Lastly, I owe Christina Kiser a thank you for helping me out in the lab.
Abstract

Any metallic element with a relatively high density as well as being toxic or poisonous when at low concentrations are considered to be “heavy metals.” Heavy metal poisoning is something one would want to avoid, but sometimes exposure could be due to something as simple as drinking water. Contamination could be done by the lead pipes it travels through. Other sources could be airborne or through contaminated food. Cosmetics though are not usually thought about when thinking of heavy metal toxins, but these impurities are thought to be unavoidable. Lead, nickel, & cadmium are among the most common metals found in cosmetics today. In lipstick alone, the FDA does not have regulations governing the level of toxic or dangerous contaminants. In one study it was found that 61% of lipsticks that they tested contained 0.65 ppm of lead\(^1\). In water, the FDA does not allow more then .005 ppm, so why is this amount so high in our makeup? Heavy metal exposure and toxins in face powders and shampoos can cause damage to the skin and hair follicles. In this study multiple lipsticks, shampoos, and face powders will be tested through ICP-OES for lead, nickel and cadmium, and results will be compared to FDA regulations in addition to calculating toxicity amount. A Raman spectrum of all the cosmetics will also be conducted and analyzed by principal component analysis (PCA)\(^2\) to visually see if the any “toxic” cosmetic grouping occurs. This could be useful for if one is unsure if their cosmetic is harmful or not, see where it groups together with other makeups.

\(^1\) Lead (Pb) Toxicity
\(^2\) Principal Component Analysis
## 1 Introduction

### 1.0 History of Toxins in Cosmetics

Cosmetic use had been dated back to 10000 BC with the Ancient Egyptians. They used what was known as the *Seven Sacred Oils* and olive oil mixed with other essences were highly esteemed in the field of cosmetics. They would use these oils to heal the body and mind, each oil targeting a specific area of the body\(^3\). Oils back then were also used as perfumes and permanent odors. Egyptians would often cover their eye with heavy dark makeup to show status. “In ancient Egypt, the focus was on the eyes, which were outlined with green or black eye paint to emphasize their size and shape. The ground pigments of green malachite, mixed with water to form as paste, were used until the middle of the Old Kingdom but were then replaced by black kohl, produced from the mineral galena, which came from the mountain regions of Sinai. Significantly, kohl had therapeutic value in protecting the eyes from infections caused by sunlight, dust, or flies\(^4\). They would also apply honey to their face and skin to help heal and fade scars. Crushed lotus flowers and the oil from various plants, like the papyrus, were also used in making these applications. These face creams held not only health benefits by protecting the skin from the sun but these cosmetics also obtained a protection from sand flies and other insects\(^5\). Though these different cosmetical techniques seem harmless, and if anything beneficial, cosmetics have greatly advanced since then.

The cosmetic industry began indulging into lipwear products, and early lipsticks were made using a toxic combination of ingredients extracted from seaweed, iodine, and among the

---

\(^3\) *Lucas, S.*

\(^4\) Quote from egyptologist Helen Strudwick

\(^5\) *Mark, J. J.*
most common, bromine mannite. The Egyptians were the first to start this lip-coloring trend, in which they would use harmful substances to achieve their desired image. Then, it was mixtures of lead, bromine mannite and iodine that were used as lipsticks. This would result in the user contracting a serious diseases or sometimes a premature death\textsuperscript{6}. It was later found that women from the Indus Valley Civilization\textsuperscript{7} would too apply lipstick regularly. Since early cosmetics were meant to show status, it was their royal members, clergy and high class citizens who would use several different types of applications. Some of them though, like the Egyptians’ lipwear, had dangerous recipes that contained poisonous ingredients that could cause serious illnesses\textsuperscript{8}. Cosmetic chemist eventually found a way to extract carmine color from beetles and ants but there is still an issues with other impurities that these products contain such as heavy metals that still resign in applications in modern times. Today the FDA\textsuperscript{9} has authority on overseeing the regulations of cosmetic products such as limits on compound concentrations of additives and colorants but they have no control on the actual regulations that govern levels of toxic or dangerous contaminants that may be found within the finished and sold product; they have no final regulations for the product’s finished levels of potential contamination\textsuperscript{10}.

Like lip wear in ancient times, face powder too consisted of dangerous ingredients. In Roman times “chalk and vinegar face creams lighten the complexion, and finely ground orris root was used in face powder.”\textsuperscript{11} In Ancient China, rice powder was commonly used to whiten

\textsuperscript{6}Sengupta, A.; Avipsha Sengupta.
\textsuperscript{7}Ancient civilization located in what is Pakistan and northwest India today, on the fertile floodplain of the Indus River and its vicinity
\textsuperscript{8}Lipstick History and Facts
\textsuperscript{9}The Food and Drug Administration
\textsuperscript{10}Analysis of Lipstick for Toxic Elements Using ICP-MS
\textsuperscript{11}Hernandez, G.
and smooth out the user’s complexion, again, to show class status\textsuperscript{12}. During Japan’s Edo Period\textsuperscript{13} many women used lead-based white powder to cover their faces. Researchers who unearthed the remains of 70 people from the ancient city of Kokura were able to determined that the women in the group had higher lead levels than the men after testing concentrations in the bones\textsuperscript{14}. In the Middle Ages, women would powder their face with flour for “high class status” but also used harsh natural bleaches, such as lye, to get rid of facial features like freckles\textsuperscript{15}. White powdered makeup also became notably theatrical. Actors who appeared in plays at Shakespeare’s Globe Theater would apply white lead and vinegar to their faces before each performance. During this era, as many before and to come, ceruse\textsuperscript{16} powders were the go-tos, no matter how much they irritated the skin. Soon enough however, these poisonous product was realized to have killed dozens of society women in addition to ruining the skin complexion of many others\textsuperscript{17}. It is safe to say throughout each generation, people would do anything to achieve a higher status, including exposing themselves to harsh chemical. Sadly though, the use of harmful chemicals in faceware did not stop there.

Near the end of the nineteenth century, face powder use began to steadily rise despite still being viewed as damaging to the skin by many. This was because the powder that was being used interfered with the face’s natural functions by blocking the skin’s pores, as well as still containing harmful ingredients like lead. Women would choose to purchase their face powders from local chemists or would buy trade-named powders but these early commercial powders

\textsuperscript{12} Kilkeary, A. M.
\textsuperscript{13} 1603–1867
\textsuperscript{14} Cohen, J.
\textsuperscript{15} Kilkeary, A. M.
\textsuperscript{16} White Lead
\textsuperscript{17} Kilkeary, A. M.
were simply a three substance mixture. Common ingredients included talc, natural starches\textsuperscript{18}, calcium carbonate (chalk), magnesium carbonate, Zinc Oxide, and more\textsuperscript{19}. Later though, titanium dioxide began to be the ingredient of choose in powders\textsuperscript{20}, which was not the most safest mineral when used improperly. If inhaled through loose products like powders or even eyeshadows and blushes, it is considered to be carcinogenic to humans\textsuperscript{21}. People were desperate to purchase the next “high quality” brand of powders in order to maintain a good appearance and so they were unaware of the possible side effects that could be harmful to them.

Lipsticks and face powders are used but are not necessary, unlike the use of cleansing products like the ones we use for our hair. Liquid shampoo is used to clean our hair by removing dirt from the hair itself and the scalp. This type of modern day shampoo though, was not invented until the late 1920s. Prior to this, people would use castile, tar or lye-based soaps to wash their hair once a month. This was due to the ingredients drying out and damaging the hair and it’s follicles if over used. Coconut, almond oil, honey and ghee (a form of purified butter) were used as hair cleansing products in 7th century India. Ingredients began to expand all over the world from the use of seeds from a cedrela tree (China, 1300s), aloe soaked in water (Philippines), and oil mixed with eggs (America, 1600s). Most of the these though seem safe and natural, something you wouldn’t have a problem using on your hair today, but what about dead lizards? Europeans used to wash their hair with dead lizards boiled in olive oil, and if that wasn’t gross enough, they also manufactures a type of hair gel that contained lizard tallow mixed with swallow droppings. It’s easy to say the modern day ingredients are not nearly as un-appealing as

\textsuperscript{18} Potato and rice
\textsuperscript{19} Washed china clay (kaolin), bismuth subchloride and subnitrate, zinc and magnesium stearate, ground orris root, and kieselguhr (diatomite)
\textsuperscript{20} J. B.
\textsuperscript{21} \textit{The Scoop on Titanium Dioxide in Cosmetics}
those, but they may be more harmful to the hair and scalp. One recent study\textsuperscript{22} found concentrations of mercury which exceeded the WHO\textsuperscript{23} limit, in synthetic and herbal shampoo. This is just one of the many studies that has recently revealed the startling amount of heavy metals that may be present in most brand products, both synthetic and herbal. Due to these studies, it is believed that if people continue to use these cosmetics, it can cause dangerous effects to the user and chances of heavy metal toxicity.

1.2 Studies Today

Heavy metal exposure in everyday life is almost unavoidable due to their natural abundance. Overtime heavy metal toxicity can have harmful results which include damage to the central nervous function, lungs, kidneys, liver, and other vital organs. Long-term exposure may lead to the development of physical, muscular, and neurological degenerative processes that mimic diseases like Alzheimer's or Parkinson's disease. Muscular dystrophy and multiple sclerosis has also been linked to heavy metal toxicity\textsuperscript{24}. Long-term contact with some of these metals may even cause cancer; so why are they showing up in stuff people come in contact with everyday like cosmetics? In a 2007 independent study\textsuperscript{25}, 33 popular brands of lipsticks were tested for lead content and 61% detected traces of the metal up to 0.65 ppm, yet the FDA has failed to take action on this matter. There is even an international ban on the intentional use of cadmium and nickel as cosmetic ingredients which was set forth by Annex II of the European Union. These metals used as cosmetic material are considered unsafe due to toxicity problems that are generated, but these compounds still remain in today’s cosmetic products\textsuperscript{26}. It has been

\textsuperscript{22} Islam, F.; Morshed, A.; Rahman, M.;...
\textsuperscript{23} World Health Organization
\textsuperscript{24} Jaishankar M, Tseten T, Anbalagan N,
\textsuperscript{25} Lead in Lipstick
\textsuperscript{26} Iwegbue CMA, Emakunu OS;...
recognized that some of these cosmetic impurities are unavoidable, as already mentioned, due to their constant nature in the atmosphere, but should still be removed whenever able to. One study looked into 35 different metals of concern that have been detected in different cosmetics, and of those, 23 were heavy metals. Daily application of these cosmetics can result in acute or even chronic heavy metal toxicity. Another study that was done by an organization called the Environmental Defence tested 49 different types of common cosmetics for 8 metals of concern. At least two were detected in every type of product and none of the metals detected though were listed on the product’s label. Below in figure A is a table of the results that were obtained from their study.

![Table of Results](image)

Figure A

27 Aldayel O, Hefne J...
28 HEAVY METAL HAZARD...
29 Mercury, Arsenic, Beryllium, Cadmium, Nickel, Lead, Selenium, Thallium
30 HEAVY METAL HAZARD...
What this study found to be most concerning though was that of the 49 products, 96 percent contained lead with amounts as high as 110 ppm, which is an order of magnitude higher than the recommended level by the FDA of <10 ppm\textsuperscript{31}. This is extremely alarming for lead has been proven to be absorbed through the skin, and so when applying these cosmetics to the face or eyes, it is like applying lead directly to these areas. The use of eye shadows that contain lead has been linked with heightened levels of the metal in children and women’s blood. This could be due to either rubbing the eyes with makeup, ingesting it off of the fingers, or through the tear duct that has come in contact with the contaminated product. Dermal absorption of lead has also been confirmed to be distributed throughout the body, and therefore the areas of application are not the only areas that will be affected. There has been no safe blood level of lead to yet be proven according to the Centers for Disease Control and Prevention. Even small amounts of lead exposure can harmful to certain bodily developments such as the brain and nervous system. These small traces of lead over time can even cause kidney damage as well has autoimmune disorders. If exposed to from the mother, small amounts can have it’s effects on a fetus in the central nervous system in children\textsuperscript{32}. What is even worse is that lead poisoning is difficult to diagnose since the side affects people exhibit are usually common day experiences like fatigue, headaches, joint pain, loss of appetite, and irritability\textsuperscript{33}. Overall, cosmetic lead poisoning has been recognized but not much has been done about it. Lead will be one of the three heavy metals of focus in this study for it seems to be potentially the most common yet most harmful.

Along with lead, nickel and cadmium are the other two other heavy metals that will be of

\textsuperscript{31} FDA’s Testing of Cosmetics for Arsenic, Cadmium,…
\textsuperscript{32} HEAVY METAL HAZARD…
\textsuperscript{33} Substance Data Sheet for…
focus. All three of these heavy metals were frequently detected in other studies that were looked at. Nickel, according to the research done in the same Environmental Defense study mentioned above, has substance list status of “toxic” in Canada but has not been banned as a cosmetic ingredient. Exposure to nickel, like lead and most heavy metals, can also cause serious health effects. Different forms of nickel like oxides, sulphides and soluble nickel compounds are even considered to be capable of causing cancer in living tissue\textsuperscript{34}. Acute exposure can cause allergic contact dermatitis or contact dermatitis with irritation. Skin contact can result in swelling, blistering and irritation around the area of contamination. Pruritus\textsuperscript{35} usually follows these symptoms sometimes leaving unwanted scaring. Over time, the area of contacted skin can thicken and peel off. Thickening of skin around the eye can even occur due to consistent application of eyeshadow or eye makeup that contains traces of nickel. Cadmium and cadmium compounds, like nickel, are considered to be carcinogenic to humans by the International Agency for Research on Cancer and are classified as known human carcinogens by the United States Department of Health and Human Services. High levels of oral exposure to cadmium has resulted in severe stomach irritation which may result in vomiting and diarrhea. Lipsticks and other lip cosmetics may not contain a high enough level of cadmium to produce these type of toxicity symptoms, but over time symptoms may begin to generate. Kidney damage, bone deformity and the ability to break bones easily have also been found to occur after long-term low level exposure to cadmium\textsuperscript{36}.

Heavy metal accumulation on the body can negatively interfere with its hormones, 

\textsuperscript{34} HEAVY METAL HAZARD…
\textsuperscript{35} An uncomfortable, irritating sensation felt anywhere on the body which urges those who experience it to scratch
\textsuperscript{36} HEAVY METAL HAZARD…
stripping the body of its nutrients and/or damaging hair follicles. Hair products, like shampoo, that contain these metals can do the same which can result in excessive hair loss or impaired hair growth\textsuperscript{37}. Shampoos that cause any hair loss due to heavy metal poisoning can last six months or longer if not treated immediately. In one study\textsuperscript{38}, traces of nine different metals, including the three metals of concern for this study (Cd, Pb, Ni), were detected in 26 brands of shampoos and other hair care products. All of these products now raise risks of exposing their consumers to these heavy metal toxicity side effects. Another study\textsuperscript{39}, this time done on facial cosmetics, tested different types of face makeup and they found that powder samples were detected with the highest concentrations of metals. In total, sixteen elements, including lead and cadmium, were found in the face powders. These powders put the user at risk for skin lesions such as hyperkeratosis, pigmentation changes and any other possible effect that has already been mentioned form heavy metal toxicity. One study done by researchers at UC Berkeley’s School of Public Health tested popular brands of lipsticks and lip glosses that can be found in common drugstores and department stores. Their results confirmed detection of lead, cadmium, chromium, aluminum and five other metals of concern in many\textsuperscript{40}.

There are numerous studies like these which confirms heavy metal, cosmetic contamination, and so why is the FDA still lacking in regulations to prevent this? The issue is not just with finding traces of metal but with the level that is detected and the effects it can cause. Concentrations of the detected metals must then be calculated with the daily use of the cosmetic product over a period of time and comparing that with existing health guidelines. It may be hard

\textsuperscript{37} Toxic Heavy Metals and Hair loss
\textsuperscript{38} Iwegbue CMA, Emakunu OS, ...
\textsuperscript{39} Aldayel O, Hefne J, ...
\textsuperscript{40} Yang, S.; Yang
to convince cosmetic users that the use of a lipstick that contains a minimal amounts of cadmium will result in cancer, but if the right calculations are done, it could be easier to warn a user that application of said lipstick will cause their bones to become brittle after so many days of exposure. Those who use lipware cosmetics will orally ingest most of it what is applied, and so we can assume that these heavy metals will slowly accumulate in our bodies, but the big question of how much still remains.

1.3 ICP-OES & Raman Intro

ICP-OES, which stands for Inductively Coupled Plasma - Optical Emission Spectrometry, is a technique used to determine a sample’s composition of elements by using plasma and a spectrometer. A sample is usually dissolved in water or prepared by acid digest. The solution is then conducted through a nebulizer into a spray chamber by a peristaltic pump. While this is happening, plasma is being generated from a cooled induction coil which contains a high frequency, alternating current flow. An alternating magnetic field is produced due to the current within the coil, accelerating electrons into a circular motion and ultimately colliding with the argon atom. As a result, ionization begins which will stabilize the plasma. The plasma is extremely hot, between 6000-7000 K, and eventually reaches 10000 K in the induction zone. The sample solution is transferred from the spray chamber and into the torch, where desolvation, atomization and ionization occur. The electrons in the sample will reach an excited state, due to thermal energy, and then drop back to the ground level. Energy is then released as light emission which is then detected and analyzed\(^\text{41}\). Every element has an own characteristic emission spectrum. The spectrometer picks up this spectrum to identify its elemental composition and

\(^{41}\text{ICP-OES,}\)
proceeds to measure the wavelength intensity, which is how the concentration is determined.

Above in figure B is an illustration on how the ICP-OES works. The spectrometer uses diffraction gratings for wavelength separation and identification of the sample’s trace elements.

Overall, this process can be broken up into four key components: (1) sample preparation (2) plasma, for excitation of electrons and photon emission (3) spectrometer, for wavelength selection (4) and the detector.
Raman spectroscopy is a spectroscopic technique used to detect different states in a molecular system, like vibrational and rotational, as well as examining the chemical composition of a material. The Raman spectrometer is an instrument that was invented based on the idea that when incident light scatters off of a molecule, it will result in a reflecting light of a different wavelength. This idea is called the Raman effect, hence the name Raman spectroscopy. Due to this, the instrument relies heavily on its laser light and its interaction with the system’s molecules. The energy of the laser photons are shifted up or down based on the molecular state it interacts with, which produces a spectrum of intensity versus shifts of wavelengths. The laser will emit radiation of a particular frequency which is then scattered when it collides with the sample. Most of the scattered radiation will have a frequency equal to the frequency of incident radiation, following the law of Rayleigh scattering. Some though, will have a frequency either higher or lower than the frequency of incident radiation. The Raman spectrometer typically detects the scattered light that has increased in wavelength, the Stokes Raman scattering, and records them as a spectrum. A molecule’s vibrational state can be analyzed through infrared (IR) spectroscopy as well as raman. In a molecule with a center of symmetry it is usually seen that raman active vibrations are IR inactive and vice-versa. This complementary nature is called the Principle of mutual exclusion and is a result of the electrical characteristic of each vibration. In general the strong IR bands of a compound are parallel to weak raman bands. For example, if a bond is strongly polarised there will be a small change in its length of vibration and will have just a small, secondary effect on polarisation. Such polarised bonds though carry these charges out during the vibrational motion, resulting in a large net

---

42 The scattering of light by particles without a change in wavelength
43 Uses interactions between infrared radiation with matter; covering a range of techniques but mostly based on absorption spectroscopy; can be used to identify chemicals
dipole moment change. Therefore, vibrations that involve polar bonds will have strong IR absorption bands and comparatively weak raman scatterers\textsuperscript{44}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig_c.png}
\caption{Figure C}
\end{figure}

Stokes lines on a raman spectrum, which can be seen above in figure C, will be generated when the frequency of incident radiation is at a higher and anti-Stokes lines when the frequency is lower\textsuperscript{45}.

1.4 PCA Intro

Principal Component Analysis (PCA) is a statistical procedure that converts a set of numerical values which may contain correlated variables into a new set of linearly uncorrelated variables called principal components. The process uses an orthogonal transformation to find principal components as vectors that can be graphed either two- or three-dimensionally. The resulting vectors, which are a linear combination of the variables and number of observations

\textsuperscript{44} Peeran, M.
\textsuperscript{45} Bumbrah, G. S.; Sharma, R. M
sets, are an uncorrelated orthogonal basis set. PCA is mostly used in exploratory data analysis or for making predictive models. It can also be used to visualize relatedness between observations. The whole idea behind PCA is to find some type of correlation between different data sets. For example, below in matrix A, there are different frequencies in Hz for each type of wavelength.

By putting these set of values through the PCA algorithm, commonalities between each set was analyzed and visual accessibility was made possible.
Above is a graph of the resulting vectors that the PCA was able to create for each type of wavelength. So what is done during the PCA process to convert this matrix into graphable vectors? A step by step example using a smaller matrix is shown below in Tables 1 and 2. This process first calculates the mean of each column and subtracts it from each number in that column. Next it finds the covariance values as well as the eigenvectors and eigenvalues of the covariance. From this, feature vectors are separated from the rest. These feature vectors are then transposed and multiplied by a transposed version of the original matrix. This then gives X, Y and Z vector values for each “sample” in the matrix which can be seen on PCA Graph K.
<table>
<thead>
<tr>
<th>Sample</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>one</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>-0.5</td>
</tr>
<tr>
<td>two</td>
<td>-0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>three</td>
<td>-0.5</td>
<td>0.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>four</td>
<td>0</td>
<td>-0.6</td>
<td>0</td>
<td>0.75</td>
</tr>
</tbody>
</table>

\[ m = \text{mean}(M) \]

\[
\begin{array}{cccc}
-0.2 & 0.175 & 0.15 & 0.0625 \\
\end{array}
\]

\[ A = M - m \]

\[
\begin{array}{cccc}
0.2 & -0.175 & -0.05 & -0.5625 \\
-0.1 & 0.325 & 0.35 & -0.0625 \\
-0.3 & 0.625 & -0.15 & -0.0625 \\
0.2 & -0.775 & -0.15 & 0.6875 \\
\end{array}
\]

\[ C = \text{cov}(A) \]

\[
\begin{array}{cccc}
0.06 & -0.1367 & -0.01 & 0.0167 \\
-0.1367 & 0.3758 & 0.0483 & -0.1646 \\
-0.01 & 0.0483 & 0.0567 & -0.0292 \\
0.0167 & -0.1646 & -0.0292 & 0.2656 \\
\end{array}
\]

\[ [V,D] = \text{eig}(C) \]

\[
\begin{array}{cccc}
0.8819 & -0.1213 & -0.3786 & 0.2534 \\
0.4181 & 0.0535 & 0.4183 & -0.8046 \\
-0.1019 & -0.9877 & -0.0006 & -0.119 \\
0.1925 & -0.0835 & 0.8256 & 0.5237 \\
\end{array}
\]

Table 1
<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample one</td>
<td>0</td>
<td>0.0672</td>
<td>-0.6733</td>
</tr>
<tr>
<td>Sample two</td>
<td>0</td>
<td>-0.3109</td>
<td>0.122</td>
</tr>
<tr>
<td>Sample three</td>
<td>0</td>
<td>0.2232</td>
<td>0.3235</td>
</tr>
<tr>
<td>Sample four</td>
<td>0</td>
<td>0.025</td>
<td>0.1678</td>
</tr>
</tbody>
</table>

Table 2
PCA Graph K
2 Experimental Procedure

2.1 Standards & Self Made Cosmetics

Before any testing began, specific brands for the three types of cosmetic in focus were picked to be tested based off of previous studies and how organic the cosmetic company is\(^\text{46}\). The first thing that had to be done was making the ICP-OES standards. With three stock solutions of Ni (10,060 ppm), Pb (10,127 ppm) and Cd (1,000 ppm), a diluted sample of 100 ppm containing all three was prepared. In a clean 100 ml plastic volumetric flask, \(\sim 3\) ml of nitric acid\(^\text{47}\) and \(\sim 5\) ml of water was combined together. Since the stock solutions did not all contain similar amounts of each metal, for this first standard, different amounts was added. With a 1000 µL micropette, 1.0 ml of the lead and nickel solutions were added to the volumetric flask. For the cadmium solution, 10 ml was taken with the use of a glass, 10 ml pipette and pipette bulb and added to the volumetric flask. The solution was then diluted with water until it reached 100 mL. The volumetric flask was then sealed and mixed by flipping the flask upside down and back until the sample is completely homogeneous\(^\text{48}\). The solution was then transferred into a clean 100 ml Erlenmeyer flask, but before doing so, a little had to be poured into the erlenmeyer flask to condition it\(^\text{49}\). Once conditioned, the Erlenmeyer flask was emptied into a waste container\(^\text{50}\) and the rest of the 100 ppm solution was poured into the conditioned flask and labeled\(^\text{51}\). After thoroughly washing out the plastic volumetric flask and glass pipette, the glass pipette was

\(\text{46}\) All material is listed in Appendix 6.1
\(\text{47}\) Any use of HNO\(_{3}\) is done under a fume hood while wearing protective laboratory gloves and eyeglasses
\(\text{48}\) Any mixture that is completely consistent in composition
\(\text{49}\) Allowing flask of use to get rid of any residue that may contaminate the sample by using the sample itself; this helps ensure quality of sample in flask
\(\text{50}\) Every flask used is labeled
\(\text{51}\) Label: Solution A, 100 ppm Ni, Pb, Cd
conditioned with the newly made 100 ppm standard solution. Next, 10 ml of the 100 ppm solution was pipetted out and inserted into the clean, plastic volumetric flask where it was again mixed with ~3 mL of nitric acid and diluted with water to 100 mL. Once mixed well, as done before, another clean 100 mL erlenmeyer flask was conditioned before transferring the solution out of the volumetric flask and labeling the erlenmeyer flask. This new standard solution is a 10% diluted sample of the first stock solution made, making it 10 ppm. This process was continued three more times, taking 10 ml from the previous solution made, until a standard solution containing 0.01 ppm (100 ppb) of lead, nickel and cadmium was produced, ultimately resulting in five different standards. In order to make sure that these solutions were accurate, they were tested with the ICP-OES along with other known solutions that contain one and/or all of the three metals of interest, within the range of 100 ppm to 100 ppb. If the known solution’s ICP-OES results correlated with the amount of metal it contains, this would validate the stock solutions that were made are precise enough to use for the cosmetic’s tests and would detect any Ni, Pb, Cd in the samples with minimal error. Once five reliable stock solutions were produced and labeled, they were sealed until needed for sample testing. More stocks were eventually made throughout the study.

The self-made cosmetics were the next thing to be made. These samples were tested as well as the name brand cosmetics to prove that cosmetics can be made, although not as nice, without any additions of heavy metals. Two different types of face powders and shampoos were made as well as a lipstick. For the lipstick, 2 tbsp of coconut oil and shea butter were melted and mixed in a double boiler with 3 tbsp of beeswax. Once all three ingredients were melted together,

---

52 Label: Solution B, 10 ppm Ni, Pb, Cd
the mixture was removed from the heat and ~½ tsp of purple mica powder and ~10 drops of lavender essential oil was added and mixed in. It was then quickly funneled into an empty cosmetic sample containers where it hardened (~1 hour). This made enough for over six containers of lipstick which was more than enough. The containers\(^{53}\) were then labeled and sealed. For one of the face powders, 2 tbsp of cornstarch and ~1 ½ tsp of cinnamon was mixed together in a mixing bowl. Once blended well, around 8 drops of lavender essential oil was added and mixed in. More oil was added until the desired texture of powder was achieved. Again, once blended well, the powder was transferred into empty cosmetic sample containers and labeled\(^{54}\). The second face powder was made by following a similar procedure but with different ingredients. By making a pair of samples with different components and giving a variety, as the cosmetic industry has plenty of, the idea that cosmetics can be made without the use metals can be proven further. For the second face powder 2 tbsp of arrowroot powder and ~1 ½ tsp of cocoa powder was mixed together and blended well. Rosemary essential oil was added and, like before, 8 drops was initially added and blended in but more was added until the proper texture was reached. Lastly ~2.5 tsp of white mica powder was added to the powder before its final blend and transferred into more empty cosmetic sample containers\(^{55}\). The two shampoos that was made had similar bases, as do most industrially produced shampoos do, but with differing side ingredients. For the first shampoo, 1/3 cup of coconut milk and liquid castile soap was combined into a labeled\(^{56}\) spray bottle and shaken well. Once the sample seemed to be blended, 20 drops of lavender essential oil was added and the bottle was shaken again to ensure

\(^{53}\) Lipstick 1

\(^{54}\) FP 1

\(^{55}\) Labeled FP 2

\(^{56}\) Shampoo 1
that all ingredients were blended. For the second shampoo, the following ingredients were combined in a mixing bowl and whisked all together until completely homogenized and smooth; 1 can of full fat coconut milk, 2 tbsp of liquid raw honey and apple cider vinegar, 2 tsp of jojoba, and 1 tsp of rosemary essential oil. The mixture was then funneled into a labeled spray bottle and shaken well. All five self made cosmetics were sealed until sample preparation.

2.2 ICP-OES Sample Preparation

Samples for all 14 of the cosmetic products were now ready to be prepared for ICP-OES testing. The shampoos and face powders had the same basic procedure for sample preparation with a slight addition in the procedure for each powder. Starting with the shampoos, on a scale tarred to zero with a weight boat on it, 0.1 grams of the sample was measured out by using a spatula. The 0.1 g of the sample was then transferred to a clean 10 ml flask where ~3 ml of nitric acid was then added. The mixture was swirled around for a bit before transferring it into a clean, plastic, 100 mL plastic volumetric flask. Here, the mixture was diluted by pouring water back into the 10 mL flask that was used and swirling that around before pouring that into the volumetric flask. This was repeated until the mixture was diluted to 100 mL. The solution was mixed well until homogeneous and used to condition a clean, sealable container before transferring and labeling. Any leftover solution from volumetric flask was poured into an appropriate waste container. This process was done for all four of the shampoo samples. For the six face powders, the same process was done except for one important addition. Once the sample had been mixed with the ~3 ml of nitric acid and diluted to 100 mL in the volumetric flask, the

---

57 Shampoo 2
58 Exact weight for each sample is listed in Appendix 6.3a
59 This is to ensure that all of the sample and nitric acid used is obtained into volumetric flask.
60 Label with what kind of sample used as well HNO₃
use of disposable pipettes and disposable pipette filters was necessary. Though more time consuming, this allowed any material from the powders that had not been completely dissolved to be filtered out of the sample that will be tested. The filtered pipette was used when conditioning the clean, sealable container it was stored in as well as when transferring the solution into said container\textsuperscript{61}. Upon completion, 10 clear, homogenous samples of the shampoo and powder products were sealed and set aside until testing.

2.3 \textit{Acid Digest}

The purchased lipsticks contain inorganic pigments like titanium dioxide and iron oxide, which are not water soluble, and so it was necessary to prepare the samples through a different technique called acid digest\textsuperscript{62}. First, 0.1 grams of a lipstick sample was measured out and transferred into a clean RBF\textsuperscript{63}, and like before, so on a scale tarred to zero with a weight boat on it. Once the sample was transferred, \textasciitilde{} 3 ml of nitric acid was added to the flask with \textasciitilde{} 3 ml of water. The water was first be transferred onto the weight boat used before being added to the RBF\textsuperscript{64}. The flask was then connected to a condenser\textsuperscript{65} and placed into a heating mantle on top of a hotplate\textsuperscript{66}. Below, in figure D, shows how this reflux set up looked like.

\textsuperscript{61} Only one pipette is necessary for each sample but the filter will need to be changed for every use
\textsuperscript{62} The process of dissolving a sample in a hot acid, or a mixture of hot acids, by a hot plate or a microwave digestion system
\textsuperscript{63} Round-Bottom Flask
\textsuperscript{64} This will help ensure that the mixture obtains all of the sample by collecting any material left on the weight boat
\textsuperscript{65} Allowing condensed vapors to drip back into the flask, minimizing loss of product due to evaporation.
\textsuperscript{66} The hotplate will be used for stirring only; heat is produced from heating mantle
The sample was stirred and heated at ~95°C, allowing it to reflux for 10-15 minutes without it boiling. The sample was cooled and ~3 more mL of HNO₃ and water was added into the RBF before covering and allowing to reflux again for 30 minutes. If browning occurred after the 30 minutes, another ~3 mL of HNO₃ and water was added. The sample continued to reflux until there was no browning occurring. Next, the solution, clear of any brown coloration that may have occurred, was allowed to evaporate until reaching ~5 ml. Once the desired amount was formed, 2 mL of water and 3 mL of a 30% H₂O₂ stock solution was added. The solution was warmed to activate the peroxide reaction and 1 ml of the 30% H₂O₂ stock solution until the

67 Continually added 5 ml of the 3% HNO₃ every 30 minutes as necessary
sample appeared to be unchanged. Lastly, 5 mL of HCL was added and the sample continued to be warmed until again, 5 mL was left. Once cooled, the solution was filtered with funnel and filter paper into a clean 100 mL plastic volumetric flask. The flask was then diluted with water until reaching 100 mL. It was then mixed well and transferred into a labeled, conditioned sealable container. These samples, as the powders’ samples did, used disposable pipettes and disposable pipette filters to condition the container and transfer the sample. Since the self made lipstick contained only organic ingredients, the use of H₂O₂ and HCL seemed to not be necessary. Following the same procedure as the name brand lipsticks, after the first allowed evaporation to 5 mL, the sample was cooled and filtered into a clean, plastic 100 mL volumetric flask where it was diluted with water to 100 mL. Once again, the sample was mixed well and transferred into a labeled, conditioned sealable container via disposable pipettes and disposable pipette filters. Once all 4 lipstick samples were prepared, they were sealed and stored with the shampoo and powder samples until testing. All labeled samples that were used in this study are shown below in figure E.
2.4  **ICP-OES & Raman**

For the ICP-OES, only two of the premade standards were used for the first round of testing, the 100 ppm and 10 ppb standards. Due to a large difference in value of Pb, Ni and Cd between the two standards\(^\text{68}\), when transferring the hose from the 100 ppm solution to the 10 ppb solution, it was not enough to just wipe the hose off. In order to avoid contamination to the 10 ppb standard, the hose was washed off a few times with water and wiped clean before placing it into standard. The hose was then be wiped and directly placed into each prepared cosmetic sample where they were scanned for any traces of nickel, lead and/or cadmium. The results for each sample is the average concentration detected from three scans taken. For the samples that detected higher traces of metal then the others, further testing with the ICP-OES was done. The Suave shampoo first appeared to contain a high amount of all three metals, and so three new samples of it was made, following the same process done in preparing that ICP-OES sample. One sample using half of the original amount used (~ 0.05), one doubling in amount (~ 0.2), and the third had a mix of 1 mL of the original sample and 1 mL of the 10 ppb stock solution, which was then diluted to 10 mL. This was done to so that if the concentration of each metal in the Suave sample was detected accurately, then the three new samples should be mathematically predicted, validating the test on the original sample. Any new samples or standards that was produced while testing was always labeled and sealed when done using. Every spectrum and numerical data was recorded and saved for further analyzation.

A Raman\(^\text{69}\) spectrum was taken and used for the creation of the PCA. When running the

\(^{68}\) 100 ppm standard solution is 10,000% larger than the 10 ppb standard solution

\(^{69}\) Raman Tutorial is listed in Appendix 5
Raman tests, the lipsticks and face powders were placed directly on the metal sample holder, while the the shampoos were transferred into a small clear, glass vials. There is no sample preparation needed. Before running the first test, the following parameters were optimized: focusing the sample, finding an appropriate laser power, and the numbers of scans to give a good spectrum. Once the parameters were found that produced a spectrum with low noise, the same or similar parameters were used other samples, adjusting it slightly according to each sample. Noisy spectra could have been a result of laser power being too high or too low or the sample being unfocused. Some samples had to have multiple scans done before producing a good spectrum. After all 14 cosmetics were measured, they were then saved individually as the spectrum file itself and as a text file. It was important to do this one by one, for if all of the spectrums were saved together as a stacked group file, the text file for each was not be attainable, which is needed for the PCA. Multiple spectra of use for one sample was stacked together to ensure consistency. This helped to see if any unnecessary noise came through on any of the spectrums.

2.5 PCA

Two separate PCAs were conducted in this study, one containing only numeric values given from the Raman spectrum and one containing both the Raman values and the concentration of each metal detected. The matrix was created on google sheets\(^70\) by copying and pasting the y-axis of each spectrum’s text file. Each column of the matrix was labeled with its corresponding sample at the top of the column. This is important to do in order to know which set of coordinates are for what samples. A sample picture of this matrix,\(^71\) Matrix B, is on the following page, showing only the first 27 rows for the full matrix contains a total of 3,3736 rows.

---
\(^70\) Excel can be used too
\(^71\) Using text files from test 2
For the first PCA, this matrix was uploaded onto Matlab where the necessary algorithm for the PCA was done. For the second, three rows at bottom were added where the average concentration of each metal that was detected from the ICP-OES was inserted for all 14 products. A 0 was entered where necessary if there was no detection during the ICP-OES tests. Now working with a new 3,739 by 14 matrix, it was again saved and uploaded to Matlab and the PCA process was conducted. The vectors that were created through the process was then three dimensionally graphed and analyzed.

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72 PCA Tutorial is listed in Appendix 3.a
3 Results

3.1 ICP-OES

The FDA published a recommended guidance for companies which includes a maximum level of 10 ppm for lead in cosmetics. This guideline applies to lipsticks, lip glosses, lip liners, eye shadows, blushes, shampoos, and body lotions\textsuperscript{73}. There is no actual regulation given by the FDA for the other two metals but Health Canada\textsuperscript{74} has a recommendation of 3 \( \mu g/g \) or less of cadmium in cosmetics, which is equivalent to 3 ppm\textsuperscript{75}. Cosmetics that contain 1 ppm or less of nickel are considered “nickel-free” and are deemed safe\textsuperscript{76} for use. These are the “safe” limits I will be using when analyzing this study’s ICP-OES results. The store bought shampoos showed traces of heavy metals. Each result of a singular test is the average of three separate scans through the ICP. The Suave shampoo sample detected 45 ppb of Cd, 42 ppb of Ni and 40 ppb of Pb. The Rahua sample showed smaller traces of each but they still detected some; 5 ppb of Cd, 3 ppb of Ni and 3 ppb of Pb. Neither of the homemade shampoos showed traces of any of the three metals, which was what to be expecting. To determine concentrations in the product as a whole, calculations relating the diluted sample to the amount used for the sample were done. On the following page is a step by step example calculation for lead in the Suave shampoo.

\textsuperscript{73} Center for Food Safety and Applied Nutrition
\textsuperscript{74} Federal Institution, a part of Health Portfolio
\textsuperscript{75} Nourmoradi H, Foroghi M…
\textsuperscript{76} Torres F, das Graças M, Melo M, Tosti A
1. Weight of product for sample: 0.0997 g

2. Diluted in 100 mL of H₂O/HNO₃ = 0.1 L

3. Concentration detected: 40 ppb = 0.040 ppm = 0.040 mg/L

4. The Concentration of Pb in shampoo (not the diluted sample): (0.040 mg/L)(0.1 L) = 0.004 mg of Pb in 0.0997 g of shampoo

5. The Concentration of Pb: (0.004 mg)/(0.0997 g) = (4 µg)/(0.0997 g) = **40.12 ppm**

This was done for every detection made for each of the three metals throughout the whole study. For Suave, along with the 40 ppm of Pb, it was also determined to contain 45 ppm of Cd and 42 ppm of Ni. This is extremely alarming when comparing these concentrations to the concentrations that have been deemed as “safe.” The Rahua was calculated to contain 4.9 ppm of Cd and 2.9 ppm of both Ni and Pb. Though the lead concentration does not exceed the FDA’s recommended limit, both the nickel and cadmium concentrations do exceed what is considered safe.

The Suave shampoo was tested multiple times with new, manipulated samples to ensure that the detected concentrations were nearly accurate. Below is a table that was created which includes predictions for what each new Suave sample should be detected with based off of the concentrations of each metal that was detected.
The concentrations detected though were unclear. The bubbles that were produced from the suave product began to clog the tubing for the ICP-OES, especially with the sample containing twice the amount of the original sample.

The powders came up relatively clean except for two small detections in the Fit Me brand, 8.7 ppb of Ni and 1 ppb of Pb, and the Bare Minerals brand with 1 ppb of Cd. Again, like the shampoos, neither homemade face powders had any detection of the three. The Fit Me face powder was calculated to contain 8.7 ppm of Ni and 1.0 ppm of Pb while the Bare Minerals face powder was determined to contain 0.97 ppm of Cd and 0.39 ppm of Ni. Both the Bare Minerals and Jane Iredale powders had no detectable Ni. None of these concentrations seem to be of any concern except the amount of nickel in the Fit Me powder by Maybelline.

For the lipsticks, after multiple trials in testing, concentrations were unable to be determined with the ICP-OES alone and so they were calculated by creating a calibration graph.

<table>
<thead>
<tr>
<th>Sample Name:</th>
<th>1</th>
<th>1/2</th>
<th>X2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of Suave Product Added (mL):</td>
<td>0</td>
<td>0.0537</td>
<td>0.2081</td>
</tr>
<tr>
<td>Suave Sample Added (mL):</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10 ppb Standard Added (mL):</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sample Volume (mL):</td>
<td>10</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Cd Concentration Prediction (ppm):</td>
<td>0.011</td>
<td>0.02326</td>
<td>0.09013</td>
</tr>
<tr>
<td>Ni Concentration Prediction (ppm):</td>
<td>0.0104</td>
<td>0.02171</td>
<td>0.08411</td>
</tr>
<tr>
<td>Pb Concentration Prediction (ppm):</td>
<td>0.01</td>
<td>0.02121</td>
<td>0.08220</td>
</tr>
</tbody>
</table>

Table 3

The concentrations detected though were unclear. The bubbles that were produced from the suave product began to clog the tubing for the ICP-OES, especially with the sample containing twice the amount of the original sample.

The powders came up relatively clean except for two small detections in the Fit Me brand, 8.7 ppb of Ni and 1 ppb of Pb, and the Bare Minerals brand with 1 ppb of Cd. Again, like the shampoos, neither homemade face powders had any detection of the three. The Fit Me face powder was calculated to contain 8.7 ppm of Ni and 1.0 ppm of Pb while the Bare Minerals face powder was determined to contain 0.97 ppm of Cd and 0.39 ppm of Ni. Both the Bare Minerals and Jane Iredale powders had no detectable Ni. None of these concentrations seem to be of any concern except the amount of nickel in the Fit Me powder by Maybelline.

For the lipsticks, after multiple trials in testing, concentrations were unable to be determined with the ICP-OES alone and so they were calculated by creating a calibration graph.
on excel and using the intensities that were recorded for each lipstick. Below, in the calibration curve C, is an example calibration curve that was created.

By using the linear equation that was produced and the intensities (y) recorded, concentrations were able to be determined. Surprisingly, the only lipstick that seemed to have intensities correlating to concentrations was the Revlon brand. It was calculated to have 0.050 ppm of Pb, 0.066 ppm of Cd and 0.029 ppm of Ni. These concentrations of lead and cadmium are the most detected throughout the whole study and raises an extreme amount of concern when calculating the concentrations of each metal in the product undiluted. These concentrations were calculated at 65.47 ppm of Cd, 28.85 ppm of Ni and 49.55 ppm of Pb. All three were well above the limits that are deemed to be “safe” and should be of concern for health effects from exposure.
<table>
<thead>
<tr>
<th>Name</th>
<th>Cd Detected (ppm)</th>
<th>Ni Detected (ppm)</th>
<th>Pb Detected (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suave</td>
<td>0.045</td>
<td>0.042</td>
<td>0.040</td>
</tr>
<tr>
<td>Rahua</td>
<td>0.005</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Shampoo 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Shampoo 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cover Girl</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Revlon</td>
<td>0.066</td>
<td>0.029</td>
<td>0.050</td>
</tr>
<tr>
<td>Burt’s Bees</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>L1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fit Me</td>
<td>0</td>
<td>0.0087</td>
<td>0.001</td>
</tr>
<tr>
<td>Bare Minerals</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Jane Iredale</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hourglass</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Face Powder 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Face Powder 2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4

Above in table 4 is the general results of concentrations determined in each of the 14 main cosmetics that were analyzed.
For the four products that detected concentrations large enough for analysis (Suave, Rahua, Fit Me, and Revlon), calibration errors were calculated for each metal following equation A below.

\[
S_x = \frac{S_y}{|m|} \sqrt{\frac{1}{k} + \frac{1}{n} + \frac{(y - \bar{y})^2}{m^2 \sum (x_i - \bar{x})^2}}
\]

Equation A

The known values for this equation are as follows. \(S_y\) is the standard deviation of the Y-values on the calibration curve (intensity); \(|m|\) is the absolute value of the slope while \(m^2\) is the squared value of the slope; \(k\) is the number of measurements done for the unknown; \(n\) is the number of data point on the calibration curve; \(\sum X_i - x^-\) is the the sum of the squared deviations from the mean of the X-values on the calibration curve; \(y\) is the Y-value of the unknown (intensity recorded); and lastly \(\bar{y}\) is the mean of the Y-values on the calibration curve. The equation’s values pertaining to the calibration curve was different for each element and the values for each unknown was different. Each value is shown below in table 5.

|       | \(S_y\)  | \(|m|\)      | \(m^2\)         | \(n\) | \(\bar{y}\) | \(\sum X_i - x^-\) |
|-------|--------|------------|----------------|------|------------|-------------------|
| Ni    | 131.1052368 | 3158.95929 | 9979023.85     | 3    | 116264.317 | 6065.9334         |
| Cd    | 876.2091141  | 13681.3192 | 187178495      | 3    | 456709.12  | 6666.00007        |
| Pb    | 5.348512669  | 1690.39312 | 2857428.89     | 3    | 62169.2    | 6065.9334         |

Table 5\(^{77}\)

\(^{77}\) Numbers calculated in google sheets, an example can be seen in Appendix pg. 74
Using these values seen in table 5 with the values that were detected and recorded, calibration error was calculated and is shown below in table 6.

<table>
<thead>
<tr>
<th>Product</th>
<th>Cd Detected</th>
<th>Cd Calibration Error</th>
<th>Ni Detected</th>
<th>Ni Calibration Error</th>
<th>Pb Detected</th>
<th>Pb Calibration Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suave</td>
<td>0.045 ppm</td>
<td>± 0.08</td>
<td>0.042 ppm</td>
<td>± 0.05</td>
<td>0.040 ppm</td>
<td>± 0.004</td>
</tr>
<tr>
<td>Rahua</td>
<td>0.01 ppm</td>
<td>± 0.08</td>
<td>0.003 ppm</td>
<td>± 0.05</td>
<td>0.003 ppm</td>
<td>± 0.004</td>
</tr>
<tr>
<td>Fit Me</td>
<td>N/A</td>
<td>N/A</td>
<td>0.009 ppm</td>
<td>± 0.05</td>
<td>0.001 ppm</td>
<td>± 0.004</td>
</tr>
<tr>
<td>Revlon</td>
<td>0.07 ppm</td>
<td>± 0.08</td>
<td>0.029 ppm</td>
<td>± 0.05</td>
<td>0.050 ppm</td>
<td>± 0.004</td>
</tr>
</tbody>
</table>

Table 6

Though these numbers seem quite small, when working with such small concentrations these are actually large error calculations. Looking at the cadmium calibration error alone, if you subtract that number from any of the concentrations detected you will receive a negative number. This though, could be due to some noise within certains standards that were used or because only three standards were used when creating the calibration curve.
3.2 Raman & PCA

Above, in Raman spec J, are example Raman spectra that was gathered during this study. This spectrum includes all 14 products. On the following page are two PCA graphs with the one on the right (PCA Graph A) using the Raman spectra only and the one on the left (PCA Graph E) using both the Raman spectra and the concentrations of each metal that was detected with the ICP-OES.

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78 All Raman Spectrums analyzed during this study can be found in the Appendix, 6.2
79 All PCA graphs analyzed during this study can be found in the Appendix, 6.4
Both include all 14 products but specifying the shampoo vectors. The PCA that included only the raman spectrum showed what was to be expected. The Shampoo samples were the points furthest out from the rest, almost forming a circle around the other samples. This makes sense due to them all have the same basic base. The Suave shampoo, which contained the most amounts of cadmium, lead, and nickel, was plotted the farthest out from the rest. This was almost the inverse result when looking at the second PCA graph. The whole idea behind the use of Raman and PCA was to try and find a new way in determining if a cosmetic is toxic or not. After analysis of multiple PCA graphs done differently, this idea cannot be conclusively proven.

| PCA Graph A | PCA Graph E |
4 Discussion

4.1 Discussion

When looking at the concentrations detected, the amount of product used has to be taken into consideration to discuss toxicity levels. These concentrations are detected in ppm, which is the same as mg/L, and by doing so allows further examination in the amounts when determining how much is absorbed. For example, the normal amount of lead that one can be exposed to daily without any adverse side effects is about 0.003 mg. Of the 0.003 mg, about ten percent is absorbed and distributed into the bones, tissues, and the central nervous system. This amount of lead that is circulating within these areas, like the soft-tissue, can remain in the body for approximately 120 days before being excreted through bile or urine. If one were to use 6 mL daily of the Suave shampoo for 120 days, they would be exposed to 28.89 mg of lead in total. This means about 0.241 mg of lead is absorbed daily and administered throughout the body’s bones and tissues, resulting with 28.44 mg of lead accumulated in these areas on the 120th day. This will lead to an over accumulation by 79,000% compared to the normal 0.036 mg that can accumulate, and with this over accumulation come the acute side effects of lead toxicity. This amount of lead absorbed is not even including other, unavoidable factors and therefore, any type of cosmetic product that has the ability to be absorbed through the skin, hair follicles, etc., should avoid heavy metal contamination.

The Fit Me face powder detected a value of 8.7 ppb of nickel, which is 0.0087 µg/g. The concentration for the whole product is 8.7 µg/g. Though this is not nearly as high as what was

---

80 Test ID: HMDB
found in the suave shampoo, there is still a need for concern. Just a small amount of skin contact with nickel can result in 77% being absorbed enter your bloodstream. After nickel is absorbed into your body it mainly goes to the kidneys but has the potential to travel through all of your organs. The most common reaction to acute toxicity from skin contact is a rash at the site of contact. Once a nickel sensitivity is developed, it will stay permanent. The average body concentration of nickel is 0.1 ppm. Nickel can stay in the body up to four weeks before being excreted through urine. If one applies about a gram of the Fit Me face powder daily for four weeks. With 77% of the nickel in the product being absorbed, after 28 days 0.1874 mg of nickel will have accumulated in places like your bloodstream and kidneys. This is about 187% higher than the average concentration in our bodies. The reference value for nickel in healthy adults is 1–3 µg/L in urine. When the 0.1874 mg is excreted, there will be a concentration of 6.693 µg/L within the urine which is more than doubles the average amount. Although these levels are not high enough to cause chronic health effects, acute effects can be produced and sensitivity to other things containing small amounts of nickel, like jewelry, can be developed.

The Revlon lipstick contains an extremely high concentration of cadmium at 65.47 µg/g. Cadmium though is not well absorbed, with about 25% of oral exposure is actually absorbed into the body, however this metal can accumulate in the body for 20 to 30 years. If one applies half a gram of this lipstick until the product has been entirely used. With 13.61 grams of lipstick in this product, it’ll take just about 28 days to use it all. Since there is 65.47 µg per gram of product, one would be exposed to 0.8911 mg of Cd, absorbing about 0.223 mg into the body. The healthy amount of cadmium that can be excreted through urine is 0.315 µg/L. After use of just one of

81 Formal Toxicity Summary…
82 Das, K. K.; Das, S. N.; Dhundasi, S. A.
83 ToxGuide for Nickel
these lipsticks about 16.37 µg/L could be excreted, about 5200% higher than the normal amount. What is even more disturbing than these factors is the oral exposure in general. It is said that exposure to 0.0005 ppm of Cd daily for one year is at a rate for chronic-duration oral exposure. By applying half a gram of the Revlon lipstick daily for one year, the body is absorbing 16.37 ppm of Cd daily. These levels are unbelievably high and chronic health effects are inevitable with daily use\textsuperscript{84}.

The three brands that were expected to contain the most amount of heavy metals was the Fit Me by Maybelline, Revlon, and Cover Girl. While doing research, these three companies in past studies, for the most part, seemed consistent with containing traces of heavy metals. What is interesting about this is that these were among the cheaper brands that were purchased. The Suave brand, which is cheaper per milliliter than Rahua, contained the most between the two. There seems to be a correlation between price and heavy metal concentration but this does not necessarily mean that the cheaper the cosmetic, the higher the concentrations. This is another reason the self made cosmetics seemed relevant for this study. Making each cosmetic was less expensive than any product that was bought. As mentioned before, though these homemade cosmetics might not be as high in quality, they still have the same basic base and no traces of Ni, Cd, or Pb were found. What was odd to find during this study was the lack of heavy metal traces in the Cover Girl lipstick product. Predictions from the start was for the Revlon and Cover Girl products to contain the most heavy metals but that only held true for Revlon.

\textsuperscript{84} ToxGuide for Cadmium
4.2 PCA Analysis

The ultimate goal of the PCA was to have some sort of guideline for deciphering if a cosmetic is toxic or not. The grouping of the products on the graph would help indicate if the cosmetic in question is harmful or not. The idea was that the cosmetics that had traces of heavy metals would group closer together and the cosmetics that had little to none would too be close together. This way, if one was uncertain about a product, they could plug their product into an algorithm and see where it is placed on the graph. For the first PCA done, the Raman spectra numerical values was all that was used. All four of the shampoos tested seem to be on the outside of the whole, surrounding the other products, but the Suave brand which detected the most traces of Ni, Pb, and Cd remained the furthest out from the rest. The PCA will make any type of correlation between uncorrelated data sets and so it makes sense that all the shampoos remained on the outside inside of two simple groupings on toxic cosmetics and safe cosmetics. This idea does seem to hold true though because of how far away the Suave is from the others. When looking at how the powders were graphed, it is hard to conclude anything since all six seem to be in the same general area. The two brands that had small detections, Fit Me and Bare Minerals, are basically in the same mix with the others. This might be because the detections, though there, were very miniscule, just like the Rahua shampoo. The Fit Me does seem to be a little further out then the rest, having a ~ 10 ppb detection for Ni, but it is the P2 that is not allowing for this to be a reasoning of its position on the graph since the P2 is even further out yet no metals were detected. Though the Revlon lipstick was a bit farther out from the majority, so was Burt’s Bees, and therefore this cannot be concluded to have been due to it’s metal concentrations. The decision to then graph the products separately based on type was then made, to see if this would
make a difference when analyzing their positions. Both the raman spectrums and the metal concentrations were included for these\(^{85}\).

The PCA of just the shampoos which included both the Raman spectra and the concentrations of each metal that was detected also showed what was to be expected. The two homemade shampoos remained close together and the Rahua not too far off, but the Suave was the furthest away. The two with no traces of metal remain the closest, the one with a small amounts detected is still close but not as close, and the one with the most amounts detected is the least closest to any of the others. While the shampoo graph had suave as somewhat of an outlier, the face powders had Jane Iredale as the farthest point away from the rest but if metal concentration had a bigger role in the PCA, the Fit Me should have been the outlier. The Lipstick’s PCA graph had no type of organization to it, for Revlon should have been a strong outlier yet its vectors remained in the middle of the four products.

4.3 Conclusion

In conclusion, five cosmetics that were tested involved concentrations of lead, nickel, and cadmium that are of concern for acute heavy metal toxicity. These product brands are Suave, Rahua, Fit Me by Maybelline, Bare Minerals, and Revlon, with Suave and Revlon containing the most of the three metals. Unfortunately, the theory behind the use of PCA in this study could not be proven for toxic cosmetics could not be deciphered through grouping of their resulting vectors. What was proven though is that certain cosmetics that are being sold online or in local drug stores do contain an alarming amount of heavy metals with no FDA regulation forbidding

\(^{85}\) PCA Graphs in Appendix 6.4b
this. These concentrations, if exposed to daily, were calculated to accumulate in the body at
above average amounts; acute toxicity can occur at these concentrations.

4.4 Further Experimentation

Out of curiosity, six more types of cosmetics were tested with the ICP-OES for cadmium,
nickel, and lead. A perfume and an eyelash enhancement serum were prepared the same way as
the shampoos were. A liquid face primer, liquid eyeliner, eyeshadow, and a mascara were
prepared the same way the powders were, with the use of a filter

None of these products
detected any traces of Cd, Pb or Ni. What was odd though was how extremely low the intensities
for these products were when recorded by the ICP-OES. Due to this. It can not be concluded if
any of these products do or do not contain any heavy metals or if there was an experimental
error. On the following page is the final table (table 7) which includes 7 of the 20 samples tested
in this study that detected at least one of the three metals of concern. It give their concentrations
detected in each sample, concentrations of the product and if they’re above or below what is
considered to be “safe”.

---

86 Exact weight for each sample is listed in Appendix 6.3c
87 Pb: <10 ppm, Cd: <3 ppm, Ni:<1 ppm
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<th>Product</th>
<th>Cd Detected (ppm)</th>
<th>Ni Detected (ppm)</th>
<th>Pb Detected (ppm)</th>
<th>pH of Product for Sample</th>
<th>Cd Concentration in Product</th>
<th>Whole “Safe” Limit</th>
<th>Ni Conc. in Product</th>
<th>Whole “Safe” Limit</th>
<th>Pb Conc. in Product</th>
<th>Whole “Safe” Limit</th>
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<td>8.038</td>
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<td>No: 41.7 ppm Over</td>
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<td>No: 39.12 ppm Over</td>
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<td>0.003</td>
<td>0.013</td>
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<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<td>7/11 Foxy Powder</td>
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<td>0.007</td>
<td>0.01</td>
<td>10.64</td>
<td>6 ppm</td>
<td>No: 6 ppm Over</td>
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<td>Two Minerals FP</td>
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<td>0</td>
<td>0.154</td>
<td>10 ppm</td>
<td>Yes: 2 ppm Over</td>
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<td>Yes: 1 ppm Over</td>
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Table 7
5 References


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6 Appendix

6.1 List of All Materials

6.1a Cosmetics Purchased

**Lipsticks:**
1. Cover Girl ~ Exhibitionist Cream Lipstick; Color - “HOT”
2. Revlon ~ Balm Stain; Shade - “Showy”
3. Burt’s Bees ~ Matte Lip Crayon; Color - “Sedona Sands”

**Face powders purchased:**
1. Maybelline ~ Fit Me Set + Smooth Powder; Color - “Buff Beige”
2. Hourglass ~ Ambient Lighting Powder; Color - “Ethereal Light”
3. Jane Iredale ~ Purepressed Base Mineral Foundation; Color - “Ivory”
4. bareMinerals ~ ORIGINAL LOOSE POWDER FOUNDATION SPF 15; Shade - “Fairly Medium 05”

**Face powders:**
1. Maybelline ~ Fit Me Set + Smooth Powder; Color - “Buff Beige”
2. Hourglass ~ Ambient Lighting Powder; Color - “Ethereal Light”
3. Jane Iredale ~ Purepressed Base Mineral Foundation; Color - “Ivory”
4. bareMinerals ~ ORIGINAL LOOSE POWDER FOUNDATION SPF 15; Shade - “Fairly Medium 05”

**Hair Shampoo:**
1. Suave ~ Rosemary + Mint Invigorating Shampoo
2. Rahua ~ Classic Shampoo

6.1b Materials for Self Made Cosmetics

**Coconut Oil**

**Shea Butter**

**Beeswax**

**Mica Powder ~ Brand: “Slice of the Moon”**
- Color: Purple
- Color: White

**Cornstarch**

**Cinnamon**

**Essential Oils**
- Lavender
- Rosemary

**Arrowroot Powder ~ Brand: “Starwest Botanicals” Organic Arrowroot Powder**

**Cocoa Powder**

**Apple Cider Vinegar**

**Coconut Milk (1 can; 13.5 oz)**

**Liquid Castile Soap**

**Liquid Raw Honey**

**Jojoba Oil**

**Water**

**Cosmetic sample containers**
Spray bottles
Mixing bowl
Measuring utensils
Heat source
2 heatable bowls
Funnel
Mixing tool; whisker

6.1c Materials for ICP-OES & Acid Digest
Nitric Acid (HNO3)
Nickel stock solution (10,000 ppm)
Lead stock solution (10,000 ppm)
Cadmium stock solution (1,000 ppm)
Water
1000 µL Micropette
10 ml glass pipette
Pipette bulb
Scale
Weight boats
100 ml erlenmeyer flasks
100 ml plastic volumetric flask
Designated waste flask
10 ml flask
Micro spatula
Small, clear, sealable, empty containers
5 ml disposable pipettes
5 ml pipette filters
Round-Bottom Flask
Hydrochloric Acid (HCl)
Funnel
Filter paper
Hot plate
30% H₂O
Heating Mantle
Water Condenser
Stir bar
Graduated Cylinder
6.2 All Raman Spectrums

Shampoos test 1 stacked: Raman Spec A
Shampoos test 2 stacked: Raman Spec B

Shampoos tests 1 & 2 stacked: Raman Spec C
Lipsticks test 1 stacked: Raman Spec D

Lipsticks test 2 stacked: Raman Spec E
Face Powders test 2 stacked: Raman Spec H

Face Powders tests 1 & 2 stacked: Raman Spec I
All samples test 1 stacked: Raman Spec J

All samples test 2 stacked: Raman Spec K
6.3  All ICP-OES Test Files, Spectrums & Exact Measurements Used

6.3a  Exact measurements Used in Sample Preparation

- Suave ~ 0.0997g
- Rahua ~ 0.1023g
- Shampoo 1 ~ 0.1222g
- Shampoo 2 ~ 0.1139g
- Fit Me ~ 0.1001g
- Bare Minerals ~ 0.1034g
- Jane Iredale ~ 0.1006g
- Hourglass ~ 0.1003g
- FP 1 ~ 0.1009 g
- FP 2 ~ 0.1017 g
- Covergirl ~ 0.1038g
- Burt’s Bees ~ 0.1030g
- Revlon ~ 0.101g
- L1 ~ 0.098g
6.3b Text Files & Spectrums

100 ppm Standard:

STD File A
STD File B
.01 ppm Standard:

STD File D
STD File E

Ni (231.604 nm), Standard 2

Ni (231.604 nm) Calibration

Intensity = 3161.1871 * Concentration + 6.0567
Correlation coefficient: 1.00000
STD File F
Face Powder Tests:

ICP-OES Table 1

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“Fit Me”:

ICP-OES File A
Shampoo Tests:

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“Suave”:

ICP-OES File B
ICP-OES File D
Lipstick Tests:

Calibration Curve Diagram A

Ni Calibration

\[ y = 3159 \times x + 425 \]

Intensity vs. Concentration (ppm)
Calibration Curve Diagram B

Cd Calibration

\[ 13675x + 1239 \]

Calibration Curve Diagram C

Pb Calibration

\[ 1690x + 182 \]
Calibration Error Calculation Example

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highlight cells B10:C12</td>
<td>x</td>
<td>y</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type =LINEST(C4:C6,B4:B6, TRUE,TRUE) and press</td>
<td>100</td>
<td>169221.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTRL+SHIFT+ENTER</td>
<td>0.01</td>
<td>195.82</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>1690.393117</td>
<td>182.4844077</td>
<td>b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Um</td>
<td>0.06867271378</td>
<td>3.984595789</td>
<td>Ub</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R^2</td>
<td>0.99999999983</td>
<td>5.348512669</td>
<td>Sy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n =</td>
<td>3</td>
<td>B16 = COUNT(B4:B6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean y</td>
<td>62169.2</td>
<td>B16 = AVERAGE(C4:C6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Xi-meanX)^2 =</td>
<td>6065.9334</td>
<td>B18 = DEVSQ(B4:B6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>measured y =</td>
<td>183.69</td>
<td>input</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k =</td>
<td>1</td>
<td>input</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>derived x</td>
<td>36.67</td>
<td>B10 = (B20-C10)/B10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.003945581346 B23 = (C12/ABS(B10))*SQRT(((1/B21)+(1/B16)+((B20-B17)^2)/(B10^2*B18)))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.3c Further Experiment Measurements

- Rapid Lash Enhancer ~ 0.1008g
- Perfume ~ 0.1020g
- Face Primer ~ 0.0993g
- Liquid Eyeliner ~ 0.1046g
- Eyeshadow ~ 0.1037g
- Mascara ~ 0.0984g
6.4  All PCA Graphs

6.4a  PCA Strictly From Raman Spectrum

PCA Graph A
PCA Graph B
PCA Graph C
6.4b  PCA From Raman Spectrum & Amount of Ni, Pb, and Cd Detected

All Products:

PCA Graph D
PCA Graph E

Shampoo 1

Shampoo 2

Suave

Rahua
PCA Graph F
Just Lipsticks:

PCA Graph G
Just Shampoos:

PCA Graphs H
Just Face Powders:

PCA Graph 1
Introduction Graphs:

PCA Graph J
PCA Graph K

Sample one

Sample two

Sample three

Sample four
6.5 *Tutorials For Instruments & PCA*

6.5a *ICP-OES*
1. Add elements: (a) Cd, wavelength- 226.502 (b) Ni, wavelength- 231.604 (c) Pb, wavelength- 220.353
2. Set conditions: (a) neb. flow- 0.9 (b) set to Manual (c) set to axial
3. Standards: (a) number of standards and their values (b) cal. error- 25%
4. Sequence number of samples and name
5. Start tests with a blank
6. Move to standards: (a) remove hose from blank solution, wipe well, place into first standard (b) do the same for each standard
7. Samples: following the same process above, move hose from one sample to the next

6.5b *Raman*
1. Place sample directly onto raman sampler container
2. Use *Omnic* and *µview*: (a) open up the Omnic software ~ program used with Raman on computer (b) open up the µview software ~ camera in raman to see sample
3. Place metal raman sampler plate into raman
4. Experimental Setup: (a) set the parameters; keep the raman open to follow the laser (b) use the µview to see and focus the sample, (c) set the laser power higher (higher the laser, less noisy spectrum)
5. Collect Data: (a) turn the white light off and the laser on (b) select raman spectrum (c) save spectrum
6. Next sample: laser must be turned off before opening raman

6.5c *PCA*
1. Upload text file from each product’s raman spectrum to excel to create one matrix; use y-axis, ignore x-axis (y-axis↓; Product→). Add any additional data to bottom of each column
2. Transpose matrix: plug in $T=M.'$
3. Calculate the mean of each column and subtract it from each number in that column: (a) plug in $m=\text{mean}(T)$ (c) proceed to then plug in $A=T-m$
4. Find the covariance: plug in $C=\text{cov}(A)$
5. Find the eigenvectors & Eigenvalues: plug in $[V,D]=\text{eig}(C)$
6. Find feature vectors: (a) plug in $V(:, 4:\# \text{of columns in matrix})=[]$ (b) $W=V.'$ (c) $B=A.'$
7. Multiply feature vector: (a) plug in $F=W*B$ (b) $FD=F.'$
8. Graph x,y,z data points from FD (final data): (a) plug in $X=FD(:,1)$ (b) $Y=FD(:,2)$ (c) $Z=FD(:,3)$ (d) scatter3(X,Y,Z)