INDIRECT DETERMINATION OF MICA VIA RUBIDIUM CONTENT AND DIRECT DETERMINATION OF HEAVY METAL LEAD IN COSMETICS

By

SAHR AYESH SALAMAH ALSHERARI

Bachelor's Degree in chemistry
Al Jouf University
Al Qurayyat, Saudi Arabia
2008

Master of Science and Technology in Chemical Analysis
and Laboratory Management
University of New South Wales
Sydney, NSW, Australia
2011

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Oklahoma State University
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Dissertation Approved:

Dr. Allen Apblett

Dissertation Adviser

Dr. Laleh Tahsini

Dr. Ziad El Rassi

Dr. Robert Matts

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Name: SAHR AYESH ALSHERARI

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Title of Study: INDIRECT DETERMINATION OF MICA VIA RUBIDIUM
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Abstract: Millions of people worldwide use cosmetics daily and some of these are unwittingly exposing themselves to dangerous levels of toxic elements such as lead. In addition to lead, mica has been widely used in cosmetics for its shimmery and reflective effect. Ground mica powder is pearlescent and satiny, qualities that have made it a common ingredient in cosmetics where it provides a shimmery, glittery, and reflective effects. Though mica is harmless as a solid, its powder or dust can cause both short- and long-term health problems. A means of identifying cosmetics that contain mica would be useful to ensure that measures are taken to avoid inhalation of potentially harmful particles. An investigation was performed on more than one hundred cosmetic samples from countries all over the world checking them for lead and for rubidium ions that commonly contained in mica. The samples were acid digested and then analyzed using an Agilent Microwave Plasma-Atomic Emission Spectrometer (MP-AES). Moreover, these samples were investigated using an EDAX Orbis X-Ray Fluorescence spectrometer as a facile rapid non-destructive method to detect these elements in cosmetics without the necessity of dissolution. This part of the investigation consisted of making lead XRF standards using silica gel and rubidium XRF standards using muscovite mica. It was found that some of the cosmetics samples did contain high concentrations of these elements. Several of the samples exceeded The US Food and Drug Administration (FDA) maximum recommended level for lead in cosmetics (10 ppm). In order to avoid the necessity of acid digestion, the XRF spectrometer was calibrated using lead-containing silica gel standards and the same was done for rubidium using mica and rubidium-containing silica gel standards. This allowed the cosmetic samples to be quantitively analyzed for lead and rubidium (mica) without destroying the samples. The XRF results were compared to the concentrations determined using MP-AES to validate the use of the XRF spectrometer for analysis of lead in cosmetics. A relationship between lead and mica has been identified that explains the mysterious existence of lead as in impurity in mica-containing cosmetics.

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CHAPTER I

INTRODUCTION

The role of cosmetics in the life of a person in the twenty-first century is significant. The desire to appear beautiful in front of others is inherited in the blood of people of all ages, different genders, and cultures. People in the past used only cosmetics that consisted of natural ingredients. On the other hand, the vast majority of the cosmetics available in the market at present consist primarily man-made materials. Although these chemicals help a person appear better, they may cause significant damage to the life of people in the long run if they contain toxic chemical. According to Bocca et al., most of the raw materials used in the manufacturing of cosmetics contain significant amounts of metals. These metals can cause skin problems and, some cases, severe diseases[1]. Bilal and Iqbal mentioned that most of the preservatives, fragrances, and surfactants used in cosmetics have health risks ranging from mild hypersensitivity to life-threatening diseases.[2] Although it is mandatory for cosmetics manufacturers to report the ingredients of their products to the consumers, most of them play tricks to avoid such mandatory requirements. They may print the ingredients on the label or pack using the smallest possible font size in order to keep them away from the notice of the consumers. Even if the consumers notice it, they may not think too much about the risk associated with such ingredients. In short, the detection of toxic elements in cosmetics is not an easy task for ordinary people.

Until five to six decades ago, the general belief among people was that cosmetics will remain only on the skin and it will never be absorbed by the body. However, modern studies have proved the ability of the skin to absorb many of the chemicals that come in contact with it. The absorption percentage could be of varying magnitude based on the nature of the chemical. Therefore, it is inevitable for consumers to have an idea of the toxicity of the cosmetic products they use. Some of the major toxic metals that can be present in cosmetics are antimony, arsenic, cobalt, nickel, mercury, cadmium, chromium, manganese, copper, and lead. According to Bilal and Iqbal, the aforementioned trace metals are used extensively in lip cosmetics in order to make the lips appear brighter[2] . Bocca et al.[1] have conducted an extensive study to learn more about the health problems generated by some of the aforementioned trace metals that are used in cosmetics for various purposes. The compound antimony sulfide is used in making cosmetics such as eye pencil, eye shadow, kohl, lipstick, makeup powder, skin cream, and soap. Antimony and its compounds have the ability to cause health problems that include respiratory disorders including pneumoconiosis, bronchitis, and emphysema and gastrointestinal problems such as abdominal pain, vomiting, and ulcers. Eye pencil, eye shadow, hair gel, and conditioner and lipstick are some of the cosmetics in which arsenic is commonly used. Long term inhalation of arsenic can cause health issues such as skin problems, lung cancer, urinary system cancer, nervous disorders, etc. Many countries including the EU countries have already banned the use of arsenic as an ingredient in cosmetics. Cadmium is another element that is commonly used in cosmetics such as eyeliner, eye pencil, eye shadow, hair conditioner, hair cream, and hair gel. It can cause tumors as well as other health problems such as lung cancer and respiratory diseases. Both chromium (VI) and chromium (III) are used in lip balm, lip gloss, lipstick, hair creams, and conditioners. They can cause contact allergies on human bodies. The reaction of cobalt on the human body has not been studied properly yet, but it is believed that this element has the ability to penetrate damaged skin more easily and cause several health problems such as itchiness, and palmar lesions. Nail polish, makeup powder, skin creams, lipstick, and eye pencil are some of the cosmetics in which cobalt is used extensively. Mercury is another chemical ingredient in cosmetics such as hair conditioner, hair gel, shampoo, shower body milk, skin creams, shower body oils, etc. It can cause renal, neurologic, and dermal problems. Nickel also used extensively in cosmetics such as eyeliner, eye pencil, face paint, hair conditioner, etc. Its use in EU countries has been prohibited due to its ability to cause health problems such as contact allergy. Lead is another chemical used in cosmetics. Many studies in the past have proved that lead has no safe exposure level. Even a small degree of exposure to lead can cause problems in the central nervous system[1].

While Bocca et al. analyzed the toxicity of metals used in cosmetics, Bilal and Iqbal studied the problems associated with the use of some chemicals and compounds in cosmetic products. Ethers like 1,4-dioxane are used extensively in products such as shampoo, mouthwash, and toothpaste. Many studies in the past have proved that this compound has the ability to cause severe diseases like breast cancer. Formaldehyde is usually used as a preservative in beauty products such as soaps, shampoos, creams, and lotions. The formaldehyde gas which is liberated from these products can cause allergies and myeloid leukemia. Moreover, it can cause significant damage to human cells such as endothelial and bronchial epithelial cells. Benzalkonium chloride is another compound used in beauty, personal care, and pharmaceutical products. Regular exposure to this compound can cause dry eye disease, burning, itching, and stinging. Imidazolidinyl urea and diazolidinyl urea are some of the other organic compounds used in cosmetics. They have the ability to liberate formaldehyde gas and can cause dermal, eye and ingestion problems, fatigue, joint pain, dizziness, nausea, etc. Organic compounds such as parabens used in cosmetics have the ability to cause several health problems including cancer and respiratory diseases. The environmental protection agencies in many countries have already banned the use of this chemical in cosmetics because of its ability to cause significant environmental problems. Phthalates, the compounds developed when phthalic acid reacts with other elements, are used as an ingredient in perfumes, lotions, nail polish, and hair care products. They can contribute to the development of endocrine disorders, reproductive problems, and carcinogenesis. Methylisothiazolinone is another organic compound that is used in beauty products such as body creams and shampoos. It can cause problems such as contact dermatitis on the human body. EU countries have already restricted the use of this chemical in cosmetics[2].

Many countries in the world have implemented regulatory measures to reduce or avoid the use of harmful chemicals and metals in the manufacturing of makeups. However, the cosmetic industry is a billion-dollar industry and it knows how to bypass all such regulatory measures. Even if the aforementioned chemicals and metals are avoided in the manufacturing of beauty products, the possibility of their existence in the form of impurities in such products cannot be ruled out completely. As mentioned earlier, many countries including EU, Canada, and US have banned the use of aforementioned eight metals in the manufacturing of beauty products[2].

At the same time, all these countries can have problems when these metals appear as impurities in cosmetic products. In some cases, these countries have allowed the restricted use of the aforementioned metals in some cosmetic products. In any case, it is a fact that harmful metals are present in most of the available cosmetic products although they may be in the form of impurities. The problem with impurities in cosmetic products is that they remain unlabeled on cosmetic products. No country can enforce a law in this regard as labelling of impurities in cosmetics is almost impossible and such an effort will cause severe problems to the billion-dollar industry. Consumers on the other hand use such products unknowingly on eyes, face, and lips as they have no way to know the amount of impurities present in those products. Above all, it will be difficult for consumers to prove that a particular beauty product has caused problems to them as they use multiple products regularly.

Although the health problems associated with the use of toxic elements in cosmetics is well known to all, the popularity of beauty products among people is not declining. Nobody wants to appear with an unpleasant look in front of others. Everybody wants to improve their looks and appearance in one way or another. The cosmetic industry, as well as the authorities, are well aware of the aforementioned human psychology. Since the detection of toxic elements in cosmetics with naked eyes is impossible, consumers are of the view that the reputed companies in this industry will not produce harmful beauty products. Ordinary consumers look for the brand name while purchasing something with a belief that reputed brands never produce harmful products

The objectives of this research are to investigate the presence of heavy metals contents and identifying their sources in cosmetics. Moreover, developing fast and dependable assessment methods for contaminated metals in cosmetics. Finally, determining the ability of XRF for quantitative and qualitative analysis.

CHAPTER II

LITERATURE REVIEW

2.1. Background Information on Cosmetics

The process of applying various materials and oils to oneself dates to at least 10,000 BC.[3] The use of cosmetics in ancient Egypt was well-documented, and Egyptians, using various herbs and poultices, crafted the modern precursors to today's mainstream cosmetics. Men and women used exotic materials such as copper and burnt almonds to form paints to use for kohl eyeliner that was widely believed to have medicinal purposes that ranged from minimizing the glare from the sun to improving eyesight[4]. Oils and ointments provided a much-needed respite from the harsh desert landscape, and as such were highly prized by all.[5] In fact, the modern word for cosmetics stems from the Latin *cosmetae*, a Roman word used to denote the various men and women whose duty it was to cover the citizens of Rome in this fashion. The use of cosmetics in modern times has a rich and varied history. At the turn of the twentieth century, cosmetics had largely fallen out of fashion. They were viewed as inappropriate for "respectable" women. Women at the time who did not wish to be classified as such were limited to simple powders and resorted to using the ends of burned matchsticks in order to darken their eyes. However, cosmetics began to take on a less sinister significance as their use was popularized by the

Russian ballet in Paris, who at the time had significant cultural influence owing to their tours around the country. The use of on-screen cosmetics in Hollywood in the United States also helped popularize cosmetics.[6] Due to the appearance of ballerinas and their heavily made up faces in the daily papers and cosmetics' gradual entrance onto the silver screen, cosmetics began to be viewed in a new light around the world. Various technological advances made cosmetic concoctions more portable over time, and gradually they came to be seen as a normal part of the grooming process.

However, as their popularity rose, so did concerns about the toxic nature of some of their components. As early as 1960 the *British Medical Journal* published journal an article titled "Safe Cosmetics"[7] and the followed-up a year later with one titled "Hazards from Cosmetics and Toilet Preparations" [8]. Both articles reflect the increasingly concerning nature of toxic ingredients in commonly available cosmetics, as well as the many detrimental effects that had begun to be seen at the time.

Recently, the nature of toxic ingredients in cosmetics has begun to take on an even greater significance, owing to greater consumer awareness of the harmful impact of cosmetics with dangerous ingredients. Cosmetic regulation varies from country to country around the globe, with some nations, such as those in the European Union, taking a harsher stance and others, like the United States, taking a more lax approach. In the United States, harmful issues reported by consumers are not monitored by the Food and Drug Administration (FDA), nor can the FDA recall products demonstrated to be harmful to consumers. [9]However, the FDA does conduct regular surveys of heavy metals including arsenic, mercury, lead, chromium, cadmium and nickel that pose a high risk of chronic toxicity after long-term exposure in humans. Low levels of these heavy metals are permitted in cosmetics despite them being banned as intentional additives. FDA testing has regularly shown a cross-section of randomly chosen cosmetics to contain far more than the allowed amounts.[10]

The FDA studies primarily employ a total dissolution method involving hydrofluoric acid, that is useful in determining the exact concentration of heavy metals within a given substance but is limited in many aspects of use[11] . This stands in contrast to regulation in the European Union, where cosmetic companies are required to report any instances of damage wrought to consumers by the use of their products as well as to prove the safety of their various ingredients prior to placing them on the market[12] . Due to lax regulation and judicial accountability of cosmetics companies, outside testing of potential contaminants is a crucial part of public health protection, such investigations help add to the body of literature currently being weighed in many countries with regard to further regulation on the topic.

2.2. Lead (Pb) in Cosmetics

Lead is a contaminant of high concern in cosmetics. Lead is toxic to humans in low doses and fatal in higher amounts. As such, there is no level of lead permitted as a direct ingredient in cosmetic products. A substantial amount of work currently exists on the topic, with most reports emphasizing the consistent evidence for the existence of lead in beauty products, the literature also to emphasizes the danger posed to consumers even if lead appears only in small concentrations. This is due to the tendency for consumers of products like lipstick to reapply it frequently throughout the day, in numbers ranging from 3-14 times per day.[13] This repeated exposure, even to low levels of lead, could have unintended consequences over time.

In response to concerning media reports detailing the presence of lead in a majority of lipsticks currently available to consumers at every price point, ranging from budget products to the more high-end. Al-Saleh and co-workers performed research that was published in article titled is "Assessment of lead in cosmetic products"[14]. This study focused on brands that had been imported to Saudi Arabia and made available at the low end of the market. Analysis were performed with an used an atomic absorption spectrometer. It was found that while most brands tested had lead concentrations below the limits mandated by the FDA, several brands came in far above them. This poses consumers with a kind of Russian roulette experience with regard to the health and safety of their cosmetic products. The researchers were especially concerned at the risk posed to pregnant mothers and those that were nursing, as contaminated products or adsorbed lead could pass directly to their children and impact their development over time. Al-Saleh and her associated researchers advocated regular testing programs be imposed by their government, as well as increased regulation to mitigate the long-term risk of lead exposure to the public.

Another study that appeared in the *Journal of Cosmetic Science* around the same time used a highly sensitive inductively coupled plasma/mass spectrometer to analyze cosmetics.[15] Researchers found from a more limited variety of lipsticks, that all the brands tested in their sample fell within amounts expected by the FDA, and as such were not a significant cause for concern. The authors tested twenty lipsticks from ten different brands, making use of lot numbers available on the lipsticks to control for quality. The authors of the study found that as long as companies conducted their business using appropriate manufacturing conditions to safe levels of lead could be maintained. They recommended in closing that companies should do just that.

A different investigation focused on the concentration of lead in kohl, a commonly used cosmetic in areas of Africa, Asia and The Middle East.[16] Researchers endeavored to purchase samples from a wide range of manufacturers located in several different countries such as Saudi Arabia and Pakistan. As is often the case with these studies, researchers found a wide range of lead contamination in the products, with some containing only a small percentage of lead while some contained more than fifty percent of lead by weight. Considering that over a third of the products tested reflected lead levels of over 50% of lead, researchers advised physicians and health workers to be on the lookout for any symptoms of lead poisoning, as well as prolonged use of kohl or similar cosmetics, as researchers may not have been previously aware of the issues.

A study that focused on the levels of lead and other heavy metals in eye shadow from China, Italy and the United States found a similar disparity in lead levels in products from different countries.[17] Overall, the report found that differences in regulation led to the largest disparities in the presence of lead in the products. They pointed out specifically that Chinese manufacturers of cosmetics were held to different standards than those in the United States and other countries. As such, the levels of lead in products from China were demonstrably higher. They recommended stringent changes in regulation regarding products which were imported from countries with lax manufacturing standards.

A Nigerian study focused on a similar region of the world also found a wide range of products to have higher levels of lead than what was permissible by law[18]. Their study focused primarily on creams and soap, with all of the products in their study found to contain some level of lead, in addition to other heavy metals such as chromium and mercury contaminants. Based on these findings, researchers urged their regulatory agencies to institute a program of sorts for removing such products from the market. However, to date, no such program has appeared in Nigeria.

A similar research effort conducted in South Africa also found that, of a selection of lipsticks randomly sampled from various stores, only 25% of samples contained safe levels of lead (as determined by the United States FDA)[19]. This poses a serious health issue for South African consumers, especially in light of the fact that a consumer might repeatedly use a contaminated product many times throughout the day. The study's authors made no specific policy recommendations, however cautioned that such products would negatively impact the female population of South Africa over the long run.

Henna is another product that has been repeatedly found to contain lead. One study on the levels of lead exposure in Saudi Arabian children from traditional henna practices might have long term impacts on the children's growth and development[20] . This was expected despite the fact that the twenty henna samples tested for lead had concentrations below amounts traditionally deemed problematic. Another study into the levels of lead exposure from henna in Morocco found similar results[21]. The authors of the study, despite not finding significant levels of lead in any of the samples tested did find that when mixed with other products in order to increase the impact of the henna, lead levels were increased to dangerous levels. The researchers concluded that, similar to the public health assessment conducted in Saudi Arabia, that lead levels could, over time, pose a significant health problem. This was especially true in the case of children.

In conclusion, lead in cosmetics has garnered a wide range of media attention as well as research on the subject. This is likely due to the fact that lead is incredibly toxic to the human body, even in small doses, and public awareness of its toxicity is high. Studies around the world have measured lead levels in products ranging from makeup, like eye shadow and lipstick, to widely used creams and deodorants. Studies have even ranged into traditional beauty practices and products such as kohl and henna. Across the board, varying levels of lead exposure were reflected based on the product, its country of manufacture and that country's specific regulation on the subject. Studies in Africa and Asia, as well as the Middle East, tended to report higher levels of lead contamination found in products across the board. In contrast, studies based in the United States and Europe, or measuring cosmetics manufactured in these countries, tended to report lower levels of lead. This likely comes as a result of varying manufacturing practices, as well as the extent to which regulations are enforced. Researchers tended to advise higher levels of regulation for consumer products, as well as increased consumer vigilance and caution where certain products were concerned.

2.3. Rubidium (Rb) in Cosmetics

Two previous investigations have identified trace amounts of rubidium in cosmetics in concentrations ranging from 2.3 to 280 ppm. G.D. Kanias investigated several types of cosmetics bought in Greece and found that eyeshadow had the highest concentrations with an average of 120 ppm and a range of 25 to 320 ppm[22]. Rouge (or blush) was found to have rubidium concentrations in the range of 10 to 130 ppm with an average of 63 ppm. Face powder had the lowest amount of rubidium with an average concentration 32 and a range from 2.3 to 84 ppm. Farrag and co-workers reported that the average concentration of rubidium in eyeshadow purchased in Jordan was 179 ppm with a range of 69 to 280 ppm.[23] Combining the data for eyeshadow yields an average value of 144 ppm for the rubidium concentration with a range from 25 to 320 ppm.

The presence of traces of rubidium in cosmetics is not a major concern since the element is remarkably non-toxic. In rats the LD_{50} for oral toxicity of rubidium chloride is 4.4 g/Kg. By comparison, the toxicity of potassium chloride and sodium chloride is higher with rat oral LD_{50}'s of 2.6 g/Kg and 3.0 g/Kg, respectively. However, the question of the source of the rubidium is intriguing since it is unlikely to be added deliberately to cosmetics. Less than four tonnes of rubidium compounds are produced per year and these are used in specialized applications. However, rubidium is the twenty-third most abundant element in the Earth's crust and occurs naturally in several minerals including leucite, pollucite, carnallite, and zinnwaldite that can contain as much as 1% by weight of rubidium oxide. The commercial source for rubidium is is lepidolite which contains between 0.3% and 3.5% rubidium. Additionally, many potassium minerals contain rubidium due to substitution for potassium. Considering the natural occurrence of rubidium, we hypothesized that the cosmetic samples that contained this element probably had a mineral ingredient common to each of them. Inspection of the ingredients of the cosmetics found positive for rubidium in this investigation revealed that mica was this common ingredient. The mica used in cosmetic is typically muscovite. J. Ahrens analyzed muscovite from several parts of the world and found an average rubidium content 968 ppm. However, there was a very large variability in the rubidium concentration with values ranging from 53 to 5852 ppm.

Mica is a common ingredient in makeup with powdery textures, such as eyeshadows, blushers, highlighters, and bronzers. Mica has shimmery and reflective effect; and it is commercially available.

Figure 2.1: Makeup (eyeshadow) contains mica[24]

Mica has been used for many years as a coloring effect that has reflective and shimmery properties in cosmetics.

Figure 2.2: Muscovite[25]

Mica itself is not toxic by skin exposure but inhalation of mica can cause fibrosis of lungs that leads to an abnormal chest x-ray, cough and shortness of breath. The CTFA International Cosmetic Ingredient Dictionary and Handbook endorses its use, and the FDA includes mica on the list of indirect food additives.[26] The Occupational Safety and Health Administration has set the legal airborne permissible exposure limit (PEL) to 20 million particles per cubic foot for mica for an 8 hour averaged exposure. Moreover, the American Conference of Governmental Industrial Hygienists (ACGIH®) and The National Institute for Occupational Safety and Health (NIOSH)[27] set a limit of 3 mg/m^3.

One objective of this study was to develop rapid and reliable assessment methods for contaminated metals in cosmetics. A study made on 140 samples that were collected randomly from the United States and Middle Eastern markets. The samples were either imported from overseas or produced locally. One analytical approach used acid for sample digestion followed by analysis of microwave plasma atomic emission spectroscopy MPAES while in second approach the samples were analyzed directly without sample preparation using x-ray fluorescence spectroscopy. All samples were analyzed by both methods.

2.4. Analytical Instrumentations

2.4.1. Microwave Plasma Atomic Emission Spectroscopy (MP-AES)

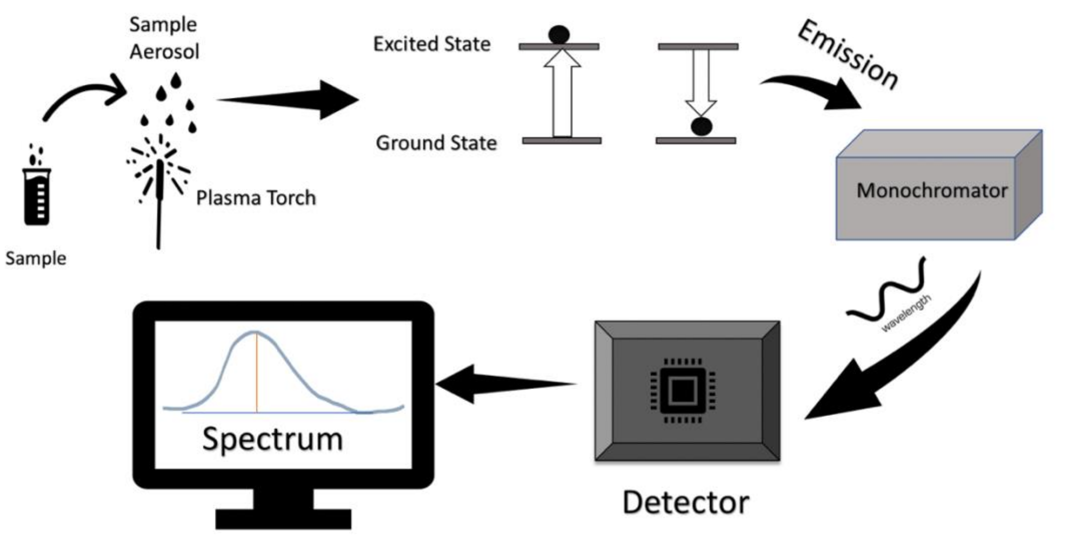

Figure 2.3: Schematic diagram of Microwave Plasma Atomic Emission Spectroscopy MPAES

Microwave Plasma Atomic Emission Spectroscopy (MPAES) is an elemental analysis method that was recently developed to enhance performance and productivity in chemical analysis while decreasing operating costs and eliminating the flammable and/or expensive gas requirements and costly consumables (e.g. hollow cathode lamps) used by other conventional elemental analysis techniques such as flame atomic absorption spectroscopy and inductively-coupled plasma atomic emission spectroscopy. An MPAES instrument is comprised of a microwave-induced plasma that is interfaced with an atomic emission spectrophotometer. MPAES is used for simultaneous determination of the concentration of multiple analytes including major and minor elements. In an MPAES instrument, microwave energy is utilized to produce a plasma discharge in nitrogen gas that can be supplied from a gas cylinder or extracted from ambient air. Samples are nebulized or otherwise volatized prior to introduction into the plasma. The sample is atomized in the plasma and electrons are promoted to excited states. As the excited atoms or ions relax to the ground state the emit characteristic wavelengths of light in the form of line spectra. The emitted light is separated into a spectrum using a spectrometer and the intensity of each target emission line is measured by the detector. Most elements can be measured in ranges as low as part per million (ppm). The MPAES technique produces superior linear dynamic range, detection limits, and analysis speed compared to conventional flame atomic absorption spectroscopy. Further, this technique produces simpler spectra than ICP-OES. The investigation reported herein, to our knowledge, is the first reported application of this novel analytical technique to a survey of the contamination of cosmetics with heavy metals. The useful detection limits and low cost of operation makes MPAES particularly suitable for this application.

2.4.2. Measuring Element Concentrations

This process is especially useful in determining the concentrations of various elements and metals and determined to be one of the best with regard to the quantification of lead levels in cosmetic products.[28] Its sensitivity allows for a high level of confidence in the results. This method has proved extremely useful to researchers aiming to adequately measure the levels of toxic elements in a range of consumer products. In one study, plasma emission spectrometry was utilized to measure the levels of titanium contamination in popular cosmetic products such as face masks.[29] Researchers found the method extremely effective at accurately determining trace amounts of the various metal elements rapidly and very precisely. The researchers further recommended its use in more routine analysis.

2.4.3. X-Ray Fluorescence (XRF) Spectroscopy

X-ray fluorescence is a widely used method for elemental analysis that is capable of rapidly identifying the presence of all elements heavier in sodium in a sample. Each chemical element has a characteristic X-ray fluorescence spectrum that is independent of the composition of the material, for instance, the characteristic X-ray fluorescence spectrum for pure lead is the same for lead chromate as for lead acetate.[30] The chemical breakdown of a sample is determined based on measurement of the secondary X-rays that are emitted from a sample after excitation by a primary X-ray source. The primary X-ray source ejects electrons from lower energy levels in an atom. Next, electrons in higher energy orbitals move to occupy the partially empty orbital while emitting an X-ray photon corresponding to the energy difference. Since the energies of emitted X-ray (i.e.

X-ray fluorescence) is unique for each element. It is possible to identify most of the elements in the periodic table.

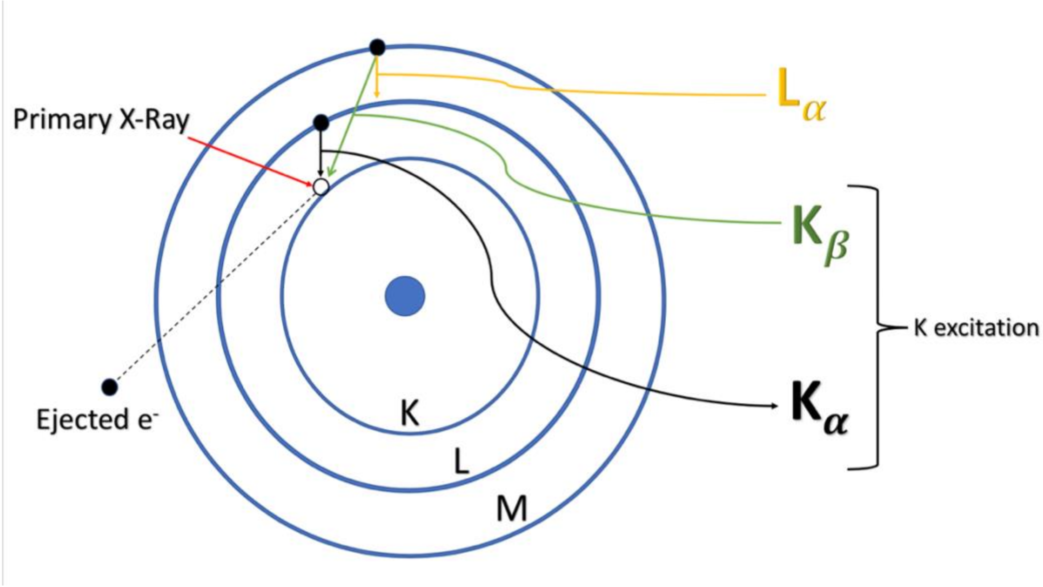

Figure 2.4: Ionization of an Element Atom in X-ray Fluorescence

An X-ray florescence spectrometer consists of two parts, a primary X-ray source and a detector.

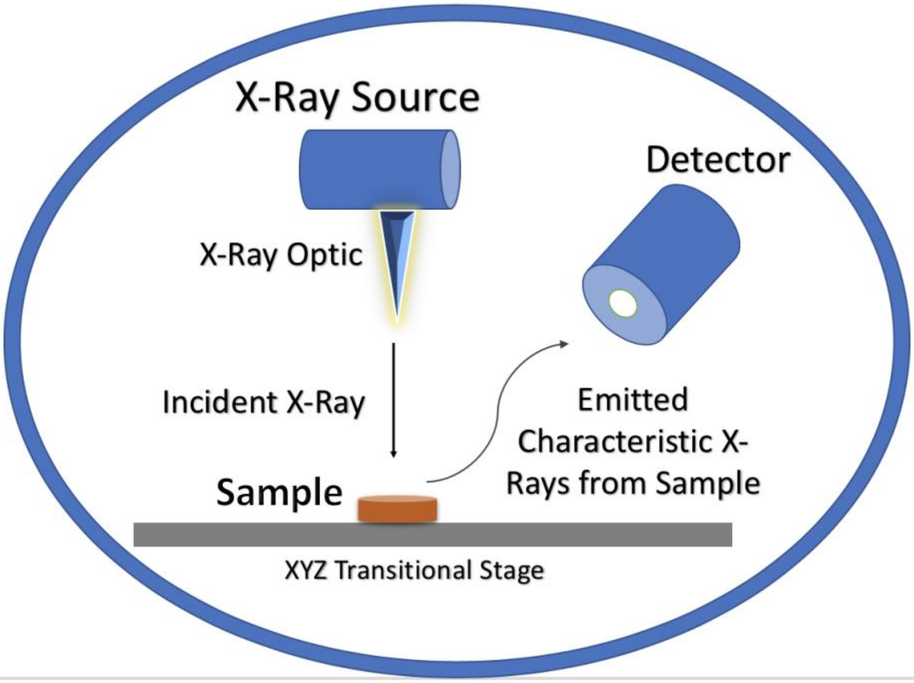

Figure 2.5: Schematic diagram of excitation spectrum measurement in X-Ray Fluorescence Spectroscopy

A typical detector is a solid state semiconductor device that is capable of simultaneously detecting and measuring the X-ray fluorescence of all elements from sodium to uranium. XRF spectroscopy is more difficult than MPAES to use for quantitative analysis due to a more limited linear range and matrix effects caused by sorption of X-rays by other elements present. However, XRF spectroscopy is an excellent tool for qualitative analysis and screening of sample. An objective of this research was to determine if XRF spectroscopy was a useful tool for screening cosmetic samples for lead concentrations above regulatory elements without the need for sample dissolution. Further, the performance of XRF spectroscopy and MPAES were compared to each other with respect to determination of lead and rubidium in cosmetic samples.

2.5. Conclusion

Cosmetics are a major part of many peoples' lives around the world on a daily basis. From their ubiquitous presence in ancient cultures to their more chaste use at the turn of the century, all the way to their current omnipresence, they make a significant impact on the culture wherever they appear. In modern times however, a greater significance has been placed on their chemical makeup and the potentially toxic elements in these products. This concern is relatively new from a historical perspective (i.e. the use of burnt and admittedly toxic matchsticks in place of eyeliner) and corresponds directly with cosmetics' rising cultural significance. Also, thanks to a rising conscientiousness where toxic elements in cosmetics are concerned, there is a greater consumer awareness of the dangers and long-term risks posed by contaminated cosmetics not only to the adult consumer but to children involved. Governmental agencies offer varying levels of regulation and testing where cosmetics are concerned. As such, more research is necessary to provide an outside reference for maintaining public safety.

Lead is an elemental component with a significant body of research into its inclusion in cosmetics. In recent years, media reports of the presence of measurable levels of lead in consumer products like lipstick have led to a widespread increase in studies aiming to measure lead concentrations. Most studies into lipstick found a wide variety in lead concentrations, with some studies concluding that all lipsticks found carried only miniscule amounts of lead that fell well within FDA guidelines (and as such were not a matter for consumer concern), while others posited that many of the samples tested were over the acceptable levels of lead contamination in consumer products. These findings tended to vary based on geographic location, with countries in Africa and Asia regularly reporting higher levels of lead in consumer products. All, however, were united in their calls for consumer caution where such products where concerned, as well as increased vigilance regarding their use. Other products that warranted extensive study were body products such as creams and kohl, which is generally used in Asia and Africa.

Studies regarding levels of rubidium in cosmetics were much more sparse, denoting a significant gap in the research.

CHAPTER III

DETERMINATION OF CONTAMINANT ELEMENTS IN COSMETICS USING X-RAY FLUORESCENCE (XRF) SPECTROSCOPY

3.1. Samples and reagents

140 cosmetic samples representing 64 different brands were collected randomly from the United States and Middle Eastern markets, (see **Table 3.1**) these samples were either imported from overseas or produced locally, stored at room temperature prior to analysis of the samples were manufactured. The majority of samples tested were made in the United States or Taiwan (25% and 24%, respectively). 13% in Europe, 1.7% were made in the Middle East, and 0.7% were produced in Canada. Some packages provide no ingredient information at all or provide incomplete information on their labels. High purity deionized water (18 MΩ·cm) obtained from a Barnstead E-Pure System was used to dilute samples and standards.

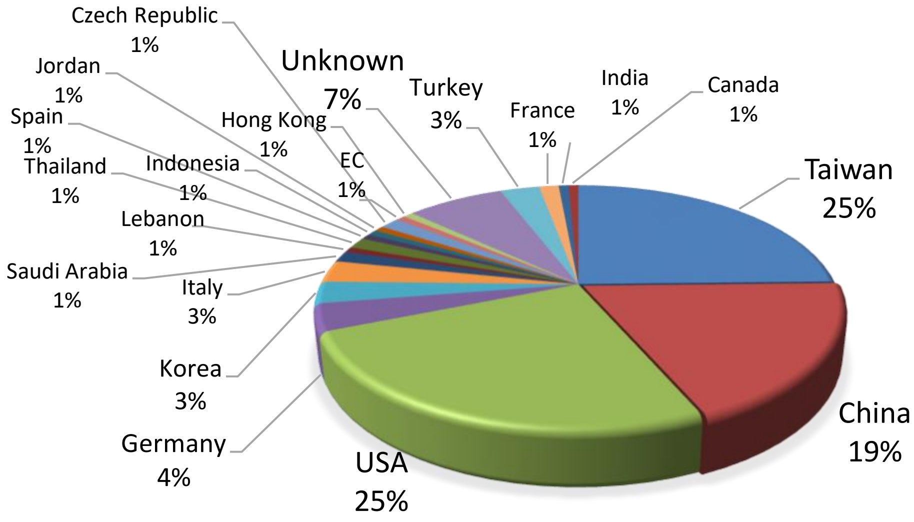

Figure 3.1: Origins of manufactures

Table 3.1: Manufacture origins of tested cosmetic samples

Origin	Number of Samples
USA	35
Taiwan	34
China	26
Unknown	12
Germany	5
Korea	4
Italy	4
Turkey	4
Saudi Arabia	2
Czech Republic	2
Thailand	2
France	2
Spain	1
Indonesia	1
Jordan	1
Lebanon	1
EC	1
Hong Kong	1
India	1
Canada	1

3.1.1. Sample Codes

Samples were labelled according to their body part applications (see appendices section). By counting the number of photons of each energy emitted from a sample, the elements present can be identified and quantitated.

3.2. Instrumentation

Orbis PC Micro-XRF Analyzers and the optimum instrument conditions used under Vacuum Mode, keV= 40, uA= 1000, and Scanning Time= 45 minutesX10 times≈ 8 hrs

3.3. Qualitative Analysis

First, all samples were screened initially to identify the presence of lead and rubidium. Later, the presence of other elements with high X-ray intensities was determined for each sample. These were then tabulated according to how many and the percentage of samples that contained the element **Table3.2.** In **Table 3.3,** these are further divided into the parts of the body where they are used.

Table 3.2: Chemical Elements and their Proportion in the Tested Cosmetic Samples.

	Element	**Number of Samples in which the Element Was Detected**	**Percentage of Samples Containing the Element**
1	Aluminum Al	113	81
2	Arsenic As	41	29
3	Barium Ba	7	5
4	Bismuth Bi	56	40
5	Bromine Br	11	8

	Element	Number of Samples in which the Element Was Detected	Percentage of Samples Containing the Element
6	Cerium Ce	1	1
7	Calcium Ca	62	44
8	Chlorine Cl	9	6
9	Cobalt Co	9	6
10	Copper Cu	27	19
11	Chromium Cr	15	11
12	Iron Fe	128	92
13	Iodine I	1	1
14	Florine F	2	2
15	Mercury Hg	19	14
16	Potassium K	77	55
17	Magnesium Mg	54	39
18	Manganese Mn	36	26
19	Molybdenum Mo	32	23
20	Nickle Ni	25	18
21	Rubidium Rb	111	79
22	Lead Pb	114	82
23	Palladium Pd	9	7
24	Phosphorus P	17	12
25	Titanium Ti	115	82
26	Tantalum Ta	115	82
27	Sulfur S	38	27
28	Silicon Si	137	98
29	Strontium Sr	2	2
30	Vanadium V	7	5
31	Tungsten W	67	48
32	Zinc Zn	35	25

Table 3.3: Chemical Elements and Their Existence in Cosmetics Based on The Body Part to Which they are Applied

	Element	**Eyes**	**Lips**	**Face**	**Nails**	**Others***
1	Aluminum Al	√	√	√	√	√
2	Arsenic As	√	√	√	√	√
3	Barium Ba		√	√		
4	Bismuth Bi	√	√	√	√	
5	Bromine Br	√	√	√	√	
6	Calcium Ca	√	√	√		√
7	Cerium Ce		√			
8	Chlorine Cl	√	√	√		√
9	Cobalt Co		√		√	
10	Copper Cu		√	√	√	
11	Chromium Cr	√	√	√	√	√
12	Iron Fe	√	√	√	√	
13	Mercury Hg	√	√	√	√	√
14	Iodine I		√			
15	Florine F			√		
16	Potassium K	√	√	√	√	
17	Magnesium Mg	√	√	√	√	√
18	Manganese Mn	√	√	√	√	
19	Molybdenum Mo	√	√	√	√	√
20	Nickle Ni		√	√	√	√
21	Rubidium Rb	√	√	√	√	√
22	Lead Pb	√	√	√	√	√
23	Palladium Pd	√	√		√	
24	Phosphorus P	√	√	√	√	
25	Titanium Ti	√	√	√	√	√
26	Tantalum Ta	√	√	√	√	√
27	Sulfur S	√	√	√	√	√
28	Silicon Si	√	√	√	√	√
29	Strontium Sr				√	
30	Vanadium V	√	√			
31	Tungsten W	√	√	√	√	
32	Zinc Zn	√	√	√	√	√

**Others such as hair dye, lotions, temporary tattoo, and body foundation*

It concludes that aluminum (Al), arsenic (As), chromium (Cr), mercury (Hg) magnesium (Mg), molybdenum (Mo), rubidium (Rb), lead (Pb), titanium (Ti), tantalum (Ta), sulfur (S), silicon (Si), and zinc (Zn) are found in all samples that applied to all body parts. However, few samples found contain cerium (Ce), barium (Ba), cobalt (Co), vanadium (V) and iodine (I) in lips products. Also, vanadium and barium (Ba) in eyes product, cobalt and strontium (Sr) in nail polish, and fluorine (F) in face products.

3.4. Quantitative Analysis

3.4.1. Synthesis of Lead-Containing Silica Gel Standards

A series of standards were made by using a lead standard solution from Inorganic Ventures with the concentration of 1000±3 μg/mL Pb in 0.5% (v/v) HNO_3. Variables amount of this solution were spiked onto 1 gram of silica gel (Aldrich 200-400 mesh, 60Å). The concentrations made were 0.2, 0.5, 1, 5, 10, 50, 100, 106, 120, 132, and 141 ppm of Pb. After drying in a fume hood overnight, they were mixed well to increase homogeneity and were stored in plastic bottles prior to XRF analysis as shown in **Figure 3.2**.

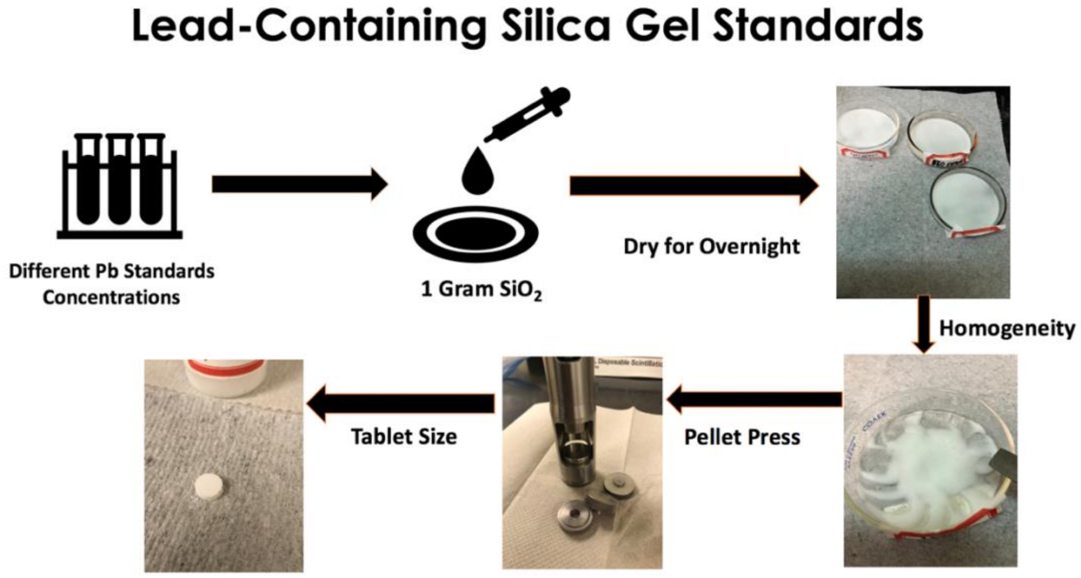

Figure 3.2: Lead-Containing Silica Gel Standards Pathway

The concentrations that were used to calibrate the XRF spectrometer were 5 ppm, 10 ppm, 50 ppm and 100 ppm. A time optimization was performed to determine the suitable scanning time for best intensity readings. The first spectra were collected at 600 seconds while at 2700 seconds was used for a second set of analyses. Base on signal to noise, the optimum scanning time (live time) chosen was 2700 seconds for one scanning point. Ten scans were averaged for each point. The resulting calibration curve is shown in *Figure 3.1* and the XRF intensities are reported. The intensities reported by the XRF spectrometer software were converted to unit counts from counts per second (CPS) using the following equation:

$$CPS \times \ live\ time\ = count$$

Where CPS is count per second

Another validation study made using mica standards to measure the accuracy of the XRF spectrometer's one-point scan and line scan modes. The latter mode has the ability to correct for inhomogeneity in the sample.

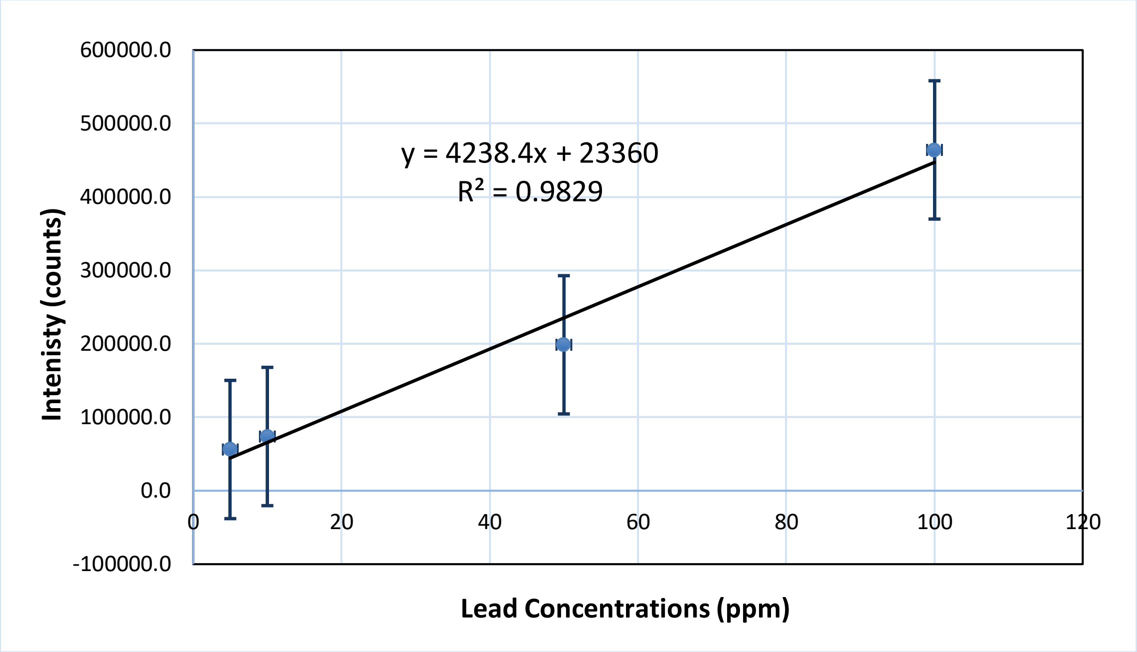

Figure 3.3: Calibration curve for lead made using lead/silica gel standards

Table 3.4: Concentrations and lead peak intensities for the standards

Lead-silica Standards	Concentration (ppm)	Intensity (counts)	Standard Deviation
Lead-silica Standard 1	5	5.61E+04	6.99E+02
Lead-silica Standard 2	10	7.38E+04	1.52E+03
Lead-silica Standard 3	50	1.99E+05	1.51E+03
Lead-silica Standard 4	100	4.64E+05	1.99E+03

The limit of detection was determined by measuring the XRF intensity in the lead peak region for blank samples made with pure silica gel. Ten spectra were collected and the standard deviation (σ) and average of the intensities were calculated. These were used to calculate the intensity associated with the limit of detection which was equal to the average intensity + 3 σ. This intensity was then converted to concentration units using calibration curve. In this manner, the limit of detection was found to be 4.25 ppm. This limit of detection is acceptable for screening of samples to determine which ones are above the FDA limit for lead of 10 ppm.

In order to probe the linearity of the response of the XRF spectrometer, standards were run with higher lead concentrations. It was found that the response was very non linear as shown in **Figure 3.3**.

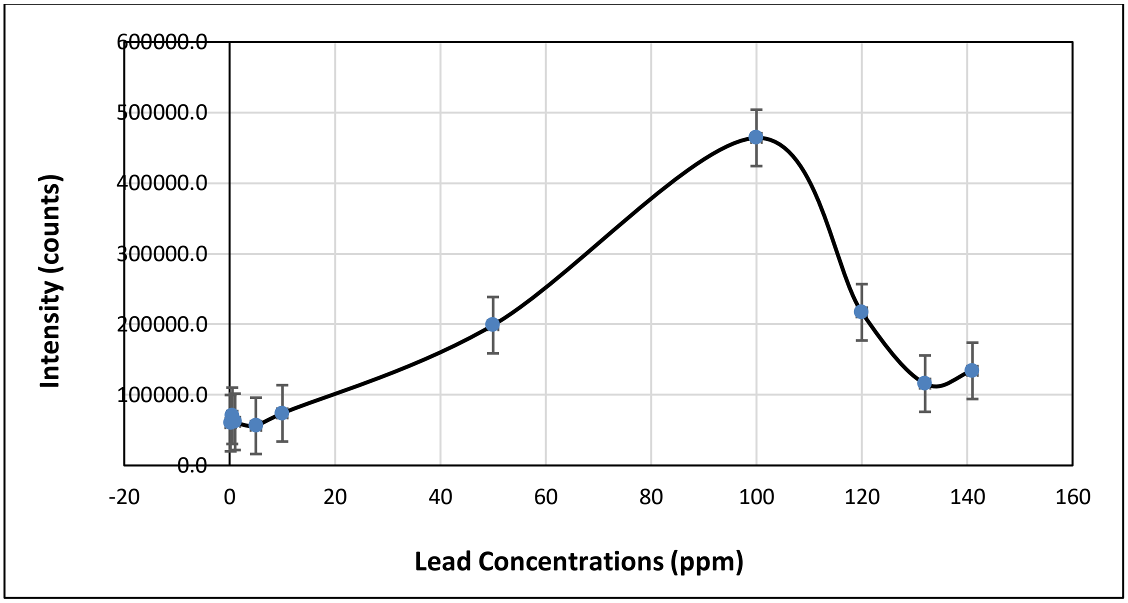

Figure 3.4: Intensity Versus Concentration for Lead/Silica Standards

The concentrations and intensities of the standards are shown in **Table 3.5**. It is evident that the response of the XRF spectrometer used in this investigation to lead is very non-linear. At higher concentrations, the intensity drops dramatically due to absorption of the lead secondary X-rays by other lead ions. This makes XRF spectroscopy less suitable for quantitative analysis since it is possible to have a particular intensity associated with two or more lead concentrations. This does not affect the ability to screen samples, but it requires additional calibration curves when the MPAES analyses indicate that the samples contain high lead concentrations above the linear range of 0 to 100 ppm of lead.

Table 3.5: Concentrations and intensities for lead/silica standards

Lead Concentration (ppm)	**Intensity**	**Standard Deviation**
0.2	5.99E+04	1.51E+03
0.5	7.04E+04	1.14E+03
1	6.18E+04	7.39E+02
5	5.61E+04	6.99E+02
10	7.38E+04	1.52E+03
50	1.99E+05	1.51E+03
100	4.64E+05	1.99E+03
120	2.17E+05	1.02E+04
132	1.16E+05	1.88E+03
141	1.34E+05	4.86E+02

For example, a calibration curve **Figure 3.5** for low lead concentrations was generated using the three lowest concentration standards (0.2, 0.5 and 10 ppm). This gave an excellent linear fit with R_2=0.9975.

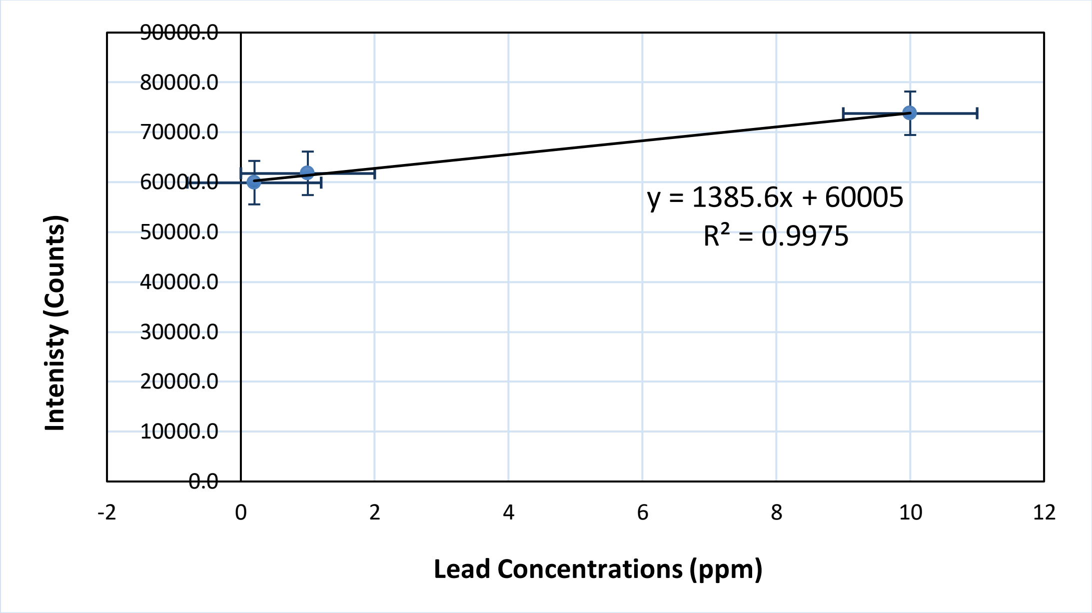

Figure 3.5: Pd Calibration Curve for Low Range

For high lead concentrations in the range of 100 to 140 ppm, another calibration curve was produced as shown in **Figure 3.6.** Again, a good linear fit was obtained.

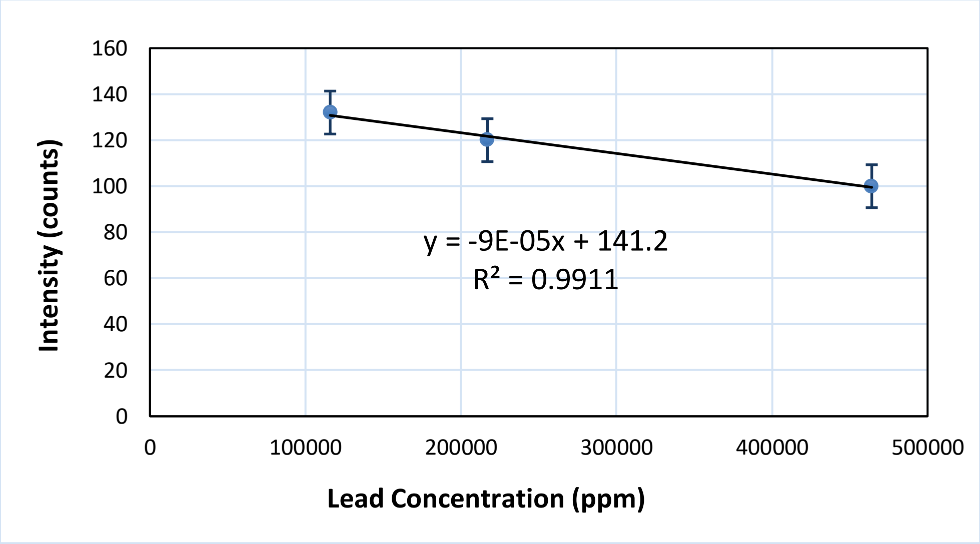

Figure 3.6: Calibration Curve for 100-140 ppm Lead.

The calibration curves were used to calculate the concentrations of lead in the cosmetic samples. The results are shown in **Table 3.6**.

Table 3.6: Lead Concentrations in Cosmetics from XRF Spectroscopy

#	**Sample Code**	**Lead concentration (ppm)**
1	SH1X1	Below LOD
2	SH1X2	0.4
3	SH1X3	1.3
4	SH1X4	Below LOD
5	SH1X5	0.4
6	SH1X6	0.6
7	SH1X7	0.3
8	SH1X8	0.3
9	SH1X9	0.2
10	SH1X10	0.5
11	SH1X11	0.4
12	SH1X12	1.1
13	SH1X13	0.5
14	SH1X14	0.5
15	SH1X15	0.8
16	SH1X16	1.0
17	SH1X17	0.2
18	SH1X18	1.6
19	B1X1	3.5
20	B1X2	1.0
21	L1X1	0.7
22	L1X2	0.7
23	L1X3	0.5
24	L1X4	0.6
25	L1X5	0.4
26	L1X6	0.4
27	L1X7	0.3
28	L1X8	0.5
29	L1X9	Below LOD
30	L1X10	Below LOD
31	L1X11	Below LOD
32	L1X12	Below LOD
33	SH2X1	0.7
34	SH2X2	0.1
35	SH2X3	0.2

#	**Sample Code**	**Lead concentration (ppm)**
36	SH2X4	2.1
37	SH2X5	1.9
38	SH2X6	1.9
39	SH2X7	0.4
40	SH2X8	5.3
41	SH2X9	0.2
42	SH2X10	3.9
43	SH2X11	2.3
44	SH2X12	1.7
45	SH2X13	5.8
46	SH2X14	3.2
47	SH2X15	1.4
48	SH2X16	2.3
49	SH2X17	1.0
50	SH3X1	1.2
51	SH3X2	5.1
52	SH4	1.0
53	SH5	3.8
54	E1	0.1
55	E2	0.2
56	E3	0.9
57	E4	0.7
58	E5	1.5
59	E6	1.5
60	E7	0.5
61	E8	0.3
62	EB1X1	0.8
63	EB1X2	8.3
64	EB2	0.5
65	B2	0.5
66	B3	1.2
67	B4	0.8
68	B5	1.3
69	F1X1	3.6
70	F1X2	2.2
71	F1X3	1.2
72	F2	10.3
73	C1	Below LOD
74	C2	2.6
75	C3	0.2
76	C4	0.2
77	C5	7.5
78	C6	0.3

#	Sample Code	Lead concentration (ppm)
79	C7	2.5
80	C8	0.1
81	C9	10
82	C10	11
83	C11X1	3.0
84	C11X2	2.3
85	C11X3	0.3
86	C11X4	5.7
87	L2	0.3
88	L3	Below LOD
89	L4	24
90	L5	6.4
91	L6	0.2
92	L7	1.7
93	L8	5.7
94	L9	5352
95	L10	2.5
96	L11	3.6
97	L12	0.2
98	L13	0.4
99	L14	1.0
100	L15	0.4
101	L16	1.0
102	L17	Below LOD
103	L18	6554
104	L19	0.6
105	L20	Below LOD
106	L21	0.1
107	L22	0.2
108	L23	0.1
109	L24	0.4
110	L25	3.2
111	L26	3.5
112	L27	4.7
113	NP1	0.1
114	NP2	1.4
115	NP3	Below LOD
116	NP4	0.2
117	NP5	0.6
118	NP6	0.1
119	NP7	0.3
120	NP8	Below LOD
121	NP11	0.2

#	Sample Code	Lead concentration (ppm)
122	NP12	1.0
123	NP13	0.2
124	NP14	0.7
125	NP15	Below LOD
126	NP16	1.1
127	NP17	0.1
128	NP18	Below LOD
129	NP19	0.3
130	H1	1.1
131	H1-2	1.3
132	H1-3	3.7
133	D1	4.2
134	LO1	1.2
135	MS1	0.4
136	MS2	1.1
137	HR	0.2
138	BC	0.3

* LOD: limit of detection

3.4.2. Synthesis of Rubidium-Containing Silica Gel Standards

A rubidium standard solution from BDH VWR analytical with a concentration of 1004±3 μg/mL Rb in 0.1% (v/v) HNO_3 was used to spike one gram of silica gel (Aldrich 200-400 mesh, 60Å), to achieve concentrations of 4 ppm, 15 ppm, 40 ppm, and 110 ppm. XRF spectroscopic analysis gave the results shown in **Table 3.7**, these were plotted to give the calibration curve shown in **Figure 3.7**.

Table 3.7: Concentrations and XRF Intensities of Rubidium/ Silica Standards

Standards	Concentrations (ppm)	Intensity (counts)	Standard Deviation
Rubidium-silica Standard 1	4.04	2.76E+04	1.38E+03
Rubidium-silica Standard 2	14.8	3.00E+04	1.63E+03
Rubidium-silica Standard 3	39.8	7.50E+04	9.85E+02
Rubidium-silica Standard 4	110	1.48E+05	5.01E+02

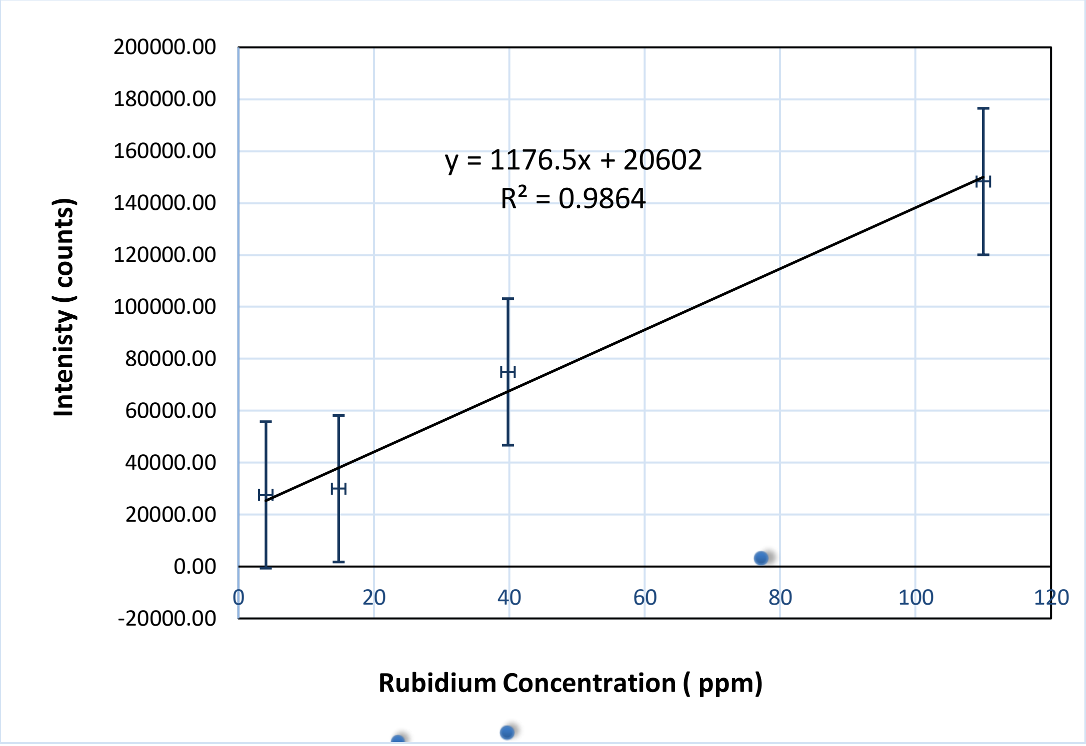

Figure 3.7: Calibration Curve for Rubidium/Silica Standards by XRF Spectroscopy

Table 3.8: Rubidium Concentrations in Cosmetics from XRF Spectroscopy

Sample Code	Rubidium Concentrations (ppm)	Standard Deviation
SH1X4	591	1.59
SH1X5	137	0.67
SH1X13	111	1.18
SH1X16	136	0.72
SH1X17	1019	0.87
SH1X18	764	1.70
B1X2	154	1.18
SH2X2	110	0.31
SH2X4	141	0.32
SH2X5	144	0.58
SH2X6	144	0.58
SH2X8	387	0.70
SH2X10	142	0.51
SH2X12	96.8	0.19
SH2X13	286	0.29
SH2X14	791	2.84
SH3X2	96.8	0.78
SH5	97.8	0.68
E5	509	1.63

Sample Code	Rubidium Concentrations (ppm)	Standard Deviation
E6	627	1.69
E7	3180	2.66
E8	2264	57.7
EB1X1	1036	7.86
EB1X2	93.9	1.11
EB2	329	3.28
F1X1	89.6	0.55
F1X2	171	4.64
F2	565	36.7
C1	187	16.4
C5	169	0.49
C10	97.3	3.50
C11X2	165	135
L4	587	1.40
L5	244	0.97
L8	88.8	0.79
L11	239	1.59
L13	1918	29.9
L17	233	0.85
L19	1915	34.6
L25	252	1.24
MS2	547	0.62

3.4.3. Preparation of Mica Standards

Mica tiles (USArtQuest) were ground to a fine powder using a Retsch Ball Mill. The powder was then spiked with the rubidium standard solution to generate standards with concentrations of 7 ppm, 10 ppm, 50 ppm, 100 ppm, and 130 ppm. XRF spectra were obtained and the resulting intensities are shown in **Table 3.9.**

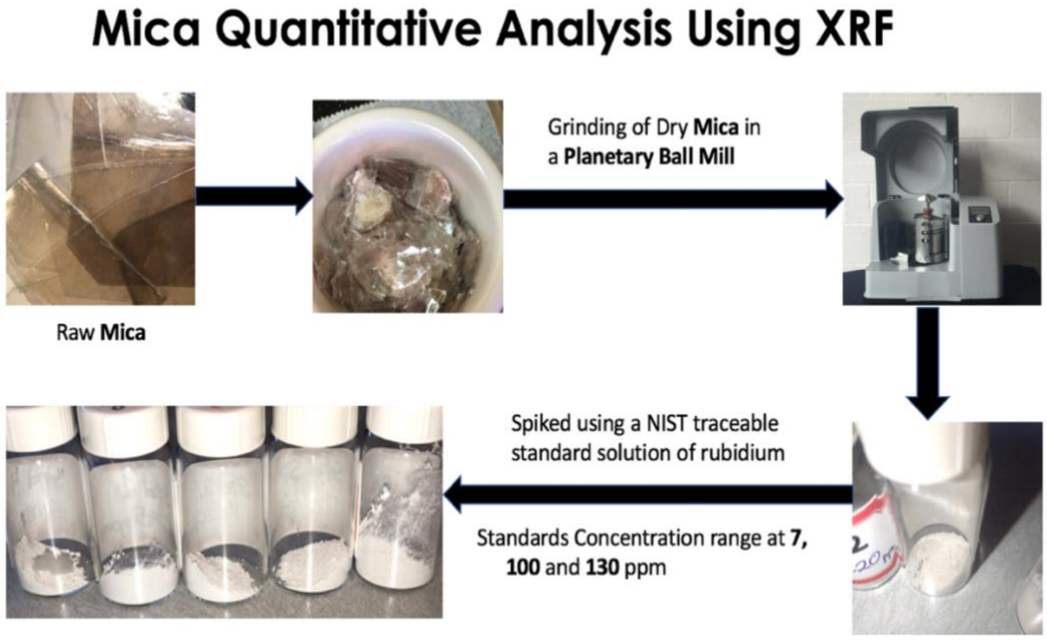

Figure 3.8: Making Mica Standards Pathway for XRF

XRF Calibration for Rubidium

Table 3.9: Concentrations and Rubidium Peak Intensities for the Mica Standards

Standards	**Rubidium Concentration (ppm)**	**Intensity (counts)**	**Standard Deviation**
Mica Standard 1	7	1.29E+05	1.78E+03
Mica Standard 2	15	1.05E+05	1.46E+03
Mica Standard 3	50	1.34E+05	3.92E+04
Mica Standard 4	100	2.68E+05	1.82E+03
Mica Standard 5	130	2.77E+05	1.83E+03

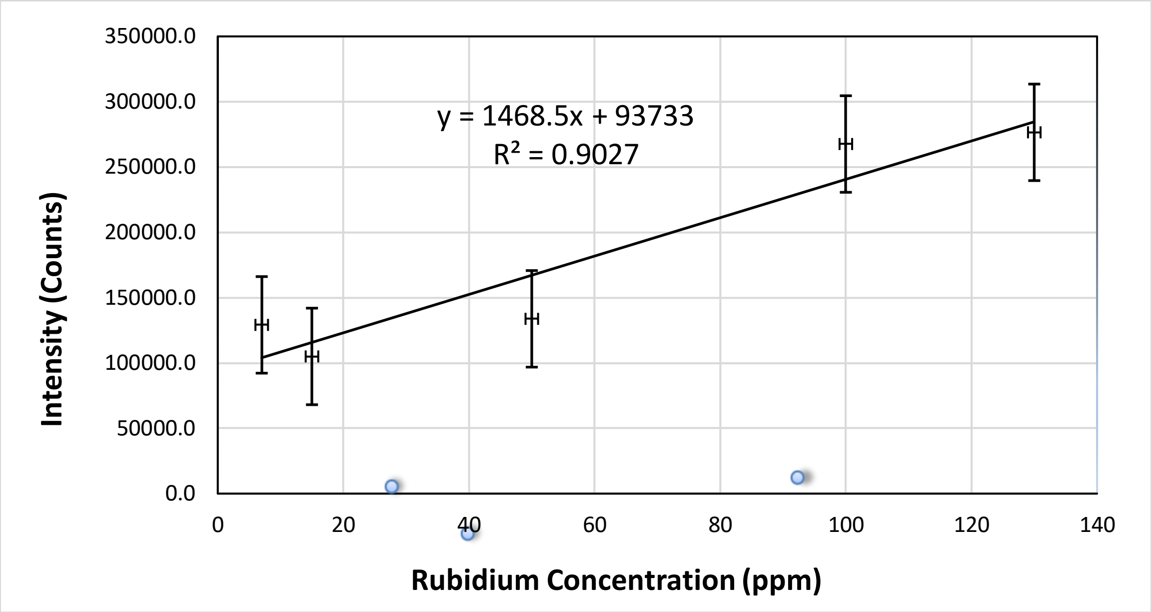

Figure 3.9: Standard Calibration Curve for Rubidium-Containing Mica

Using the calibration curve and the XRF spectroscopic results, the concentration of rubidium in cosmetics were calculated. The results are produced in **Table 3.10.**

Table 3.10: Rubidium Concentrations in Cosmetics

Sample Code	Rubidium Concentrations (ppm)	Standard Deviation
SH1X4	591	1.59
SH1X5	137	0.67
SH1X13	111	1.18
SH1X16	136	0.72
SH1X17	1019	0.87
SH1X18	764	1.70
B1X2	154	1.18
SH2X2	110	0.31
SH2X4	141	0.32
SH2X5	144	0.58
SH2X6	144	0.58
SH2X8	387	0.70
SH2X10	142	0.51

Sample Code	Rubidium Concentrations (ppm)	Standard Deviation
SH2X12	96.8	0.19
SH2X13	286	0.29
SH2X14	791	2.84
SH3X2	96.8	0.78
SH5	97.8	0.68
E5	509	1.63
E6	627	1.69
E7	3180	2.66
E8	2264	57.8
EB1X1	1036	7.86
EB1X2	93.9	1.11
EB2	329	3.28
F1X1	89.6	0.55
F1X2	171	4.64
F2	565	36.8
C1	187	16.5
C5	169	0.49
C10	97.3	3.50
C11X2	165	135
L4	587	1.40
L5	244	0.97
L8	88.8	0.79
L11	239	1.59
L13	1918	29.8
L17	233	0.85
L19	1915	34.6
L25	252	1.24
MS2	547	0.62

The limit of detection calculated for rubidium was determined to be 8.14 ppm using the average signal and the standard deviation of ten experiments performed with pure silica gel as the blank sample. The calibration curve was used to calculate the limit of detection from the average number of counts plus three times the standard deviation. The instrument conditions used were:

Number of points was 512, vacuum scanning mode, Dwell (mS)= 100, Data type=ROI, Amp time was 0.8 μS, and without any shutter-filter.

At the beginning, time optimization done to determine best intensity reading by Line Scanning for a raw mica standard for 6 mSec, 37 mSecs and 261 mSecs. Therefore 261 mSec of 1000 Dwell (mS) was the best intensity result.

Table 3.11: Concentrations and Rubidium Peak Intensities for The Mica Standards via Line Scan

Standards	**Rubidium Concentration from MP-AES Analysis (ppm)**	**XRF Intensity from Line Scan Analysis (counts)**
Mica Standard 1	7.0	5.23E+05
Mica Standard 2	14	4.10E+05
Mica Standard 3	40	4.54E+05
Mica Standard 4	80	4.60E+05
Mica Standard 5	98	5.02E+05

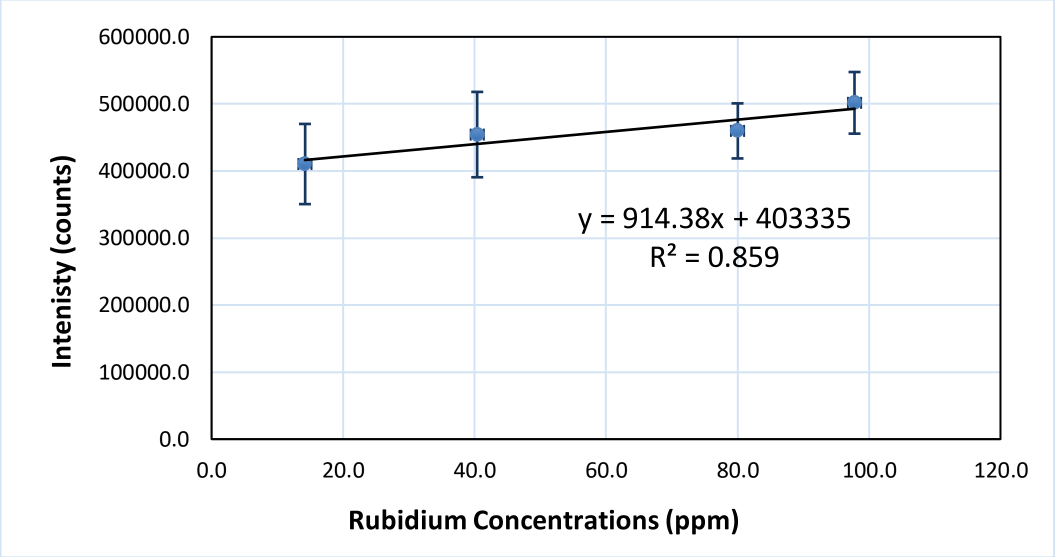

Figure 3.10: Standard Calibration Curve for Rubidium Uses The XRF Line Scan Mode In Mica Standards.

As it has seen that line scan was not good enough and less accurate than one-point scan. Moreover, the same line scan done for rubidium/silica standards and the calibration was so poor.

3.5. Rubidium in Mica

Intensity of mica (muscovite) = 129163±1620 counts = 4±0.7 ppm

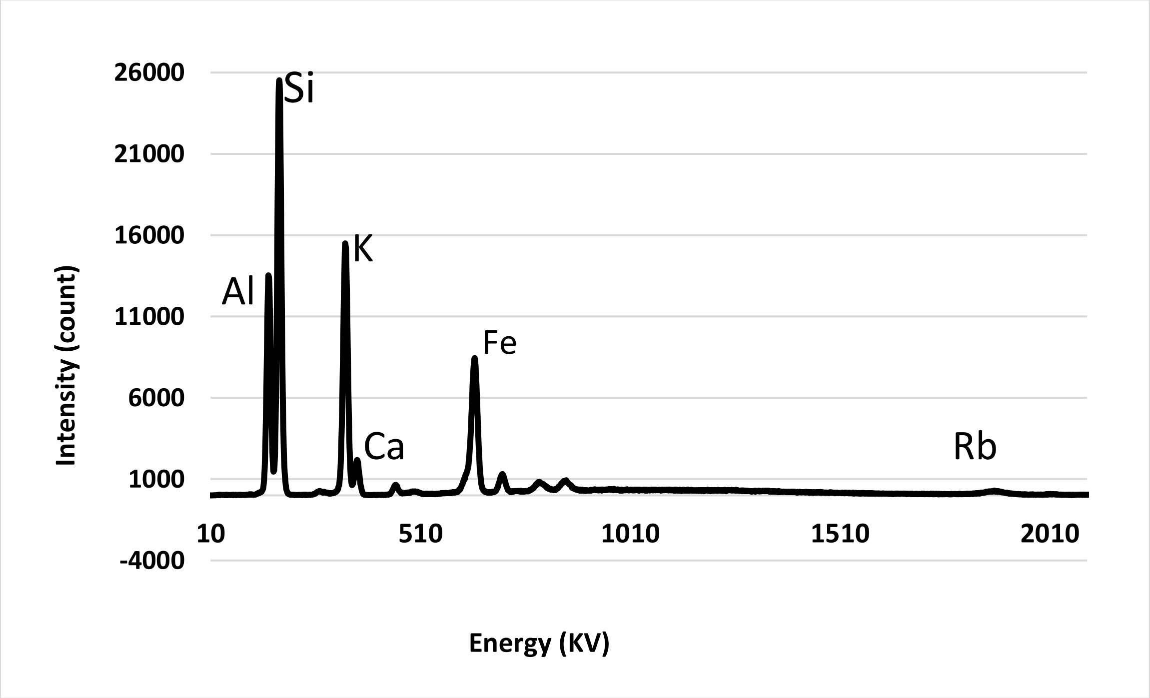

Figure 3.11: XRF Spectrum of Mica Standard

Concentration of mica (muscovite) was 6.8 ppm via MPAES. Furthermore, there are 41 samples contain rubidium measured via XRF mica calibration curve as shown in **Table 3.12**.

Table 3.12: XRF Positive Results for Rubidium Concentrations in Cosmetics

#	**samples**	**Intensity (counts)**	**Concentration (mg/kg)**	**Standard Deviation**
1	SH1X4	7.16E+05	467	1.6
2	SH1X5	1.81E+05	45	0.7
3	SH1X13	1.51E+05	21	1.2
4	SH1X16	1.81E+05	45	0.7
5	SH1X17	1.22E+06	865	0.9
6	SH1X18	9.20E+05	628	1.7
7	B1X2	2.02E+05	61	1.2
8	SH2X2	1.49E+05	20	0.3
9	SH2X4	1.86E+05	49	0.3
10	SH2X5	1.89E+05	51	0.6
11	SH2X6	1.89E+05	51	0.6
12	SH2X8	4.76E+05	277	0.7
13	SH2X10	1.87E+05	50	0.5
14	SH2X12	1.35E+05	8	0.2
15	SH2X13	3.57E+05	184	0.3
16	SH2X14	9.51E+05	653	2.84
17	SH3X2	1.35E+05	8	0.78
18	SH5	1.36E+05	9	0.68
19	E5	6.19E+05	390	1.63
20	E6	7.58E+05	500	1.69
21	E7	3.76E+06	2871	2.66
22	E8	2.68E+06	2020	58
23	EB1X1	1.24E+06	880	7.9
24	EB1X2	1.31E+05	5	1.1
25	EB2	4.07E+05	223	3.3
26	F1X1	1.26E+05	1	0.6
27	F1X2	2.22E+05	77	4.6
28	F2	6.85E+05	442	37
29	C1	2.41E+05	92	16
30	C5	2.20E+05	75	0.5
31	C10	1.35E+05	8	3.5
32	C11X2	2.14E+05	71	135
33	L4	7.11E+05	463	1.4
34	L5	3.07E+05	144	0.9

#	samples	Intensity (counts)	Concentration (mg/kg)	Standard Deviation
35	L8	1.25E+05	0.61	0.8
36	L11	3.02E+05	140	1.6
37	L13	2.28E+06	1699	29
38	L17	2.95E+05	134	0.9
39	L19	2.27E+06	1696	35
40	L25	3.17E+05	152	1.2
41	MS2	6.64E+05	426	0.6

3.6. Conclusion

The quality of XRF measurements was evaluated by different statistical calculations. This is mainly the calculation of the correlation coefficient (r) or the coefficient of determination (r_2). The calculation of the standard deviation (SD) and the relative standard deviation (%RSD = SD / Mean*100), were all found reasonable. It can be seen that linear regression of rubidium-silica standards is slightly better than mica standards by 0.0192 for value of r_2.

CHAPTER IV

DETERMINATION OF CONTAMINATION OF COSMETICS USING MICROWAVE PLASMA ATOMIC EMISSION SPECTROSCOPY

All samples were digested using a wet digestion method applied to 0.25 grams of raw cosmetic sample treated with 10 mL of concentrated nitric acid HNO_3 (ACS reagent grade) at 80 °C. The digested sample was diluted using 10 mL of deionized water and was then filtered using a 25 mm syringe filter with 0.2 μm nylon membrane. Alternatively, it was centrifuged for 15 minutes to separate the undissolved particles. Lead standard solution from Inorganic Ventures at the concentration of 1000±3 μg/mL Pb 0.5% (v/v) HNO_3, and rubidium standard solution from BDH VWR analytical at the concentration of 1004±3 μg/mL Rb 0.1% (v/v) HNO_3 were used to make a series of diluted standards to calibrate the MPAES. The digested cosmetic samples were analyzed for lead (Pb) and rubidium (Rb) by MPAES with 3-14 replicates per sample. The linearity of the method was good in the range 0.01-50 ppm, with a correlation coefficient of 0.9999. The cosmetic samples were diluted into this range for analysis. The limit of detection for lead was 3.61 ppb (n=20) via MPAES.

4.1. Lead (Pb) Concentrations in Cosmetics

Table 4.1: MPAES Lead Concentrations for the Cosmetic Samples

#	Sample Code	Lead concentration ug/g (ppm)	Standard Deviation	Percentage
1	SH1X2	1.91	0.33	1.91E-06
2	SH1X3	1.43	0.50	1.43E-06
3	SH1X5	2.01	1.18	2.01E-06
4	SH1X6	2.45	0.66	2.45E-06
5	SH1X7	1.90	0.66	1.90E-06
6	SH1X8	1.32	0.36	1.32E-06
7	SH1X10	1.74	0.27	1.74E-06
8	SH1X11	1.64	0.96	1.64E-06
9	SH1X12	1.30	0.44	1.30E-06
10	SH1X13	2.20	1.20	2.20E-06
11	SH1X14	3.38	0.42	3.38E-06
12	SH1X15	2.99	1.55	2.99E-06
13	SH1X17	7.79	2.75	7.79E-06
14	B1X1	2.61	0.47	2.61E-06
15	B1X2	5.05	0.57	5.05E-06
16	L1X1	0.66	0.24	6.58E-07
17	L1X2	2.32	3.47	2.32E-06
18	L1X3	0.86	0.45	8.58E-07
19	L1X4	2.72	2.39	2.72E-06
20	SH2X1	2.39	1.59	2.39E-06
21	SH2X3	2.49	1.72	2.49E-06
22	SH2X4	1.79	1.09	1.79E-06
23	SH2X5	1.43	1.05	1.43E-06
24	SH2X6	1.93	1.17	1.93E-06
25	SH2X8	1.16	0.29	1.16E-06
26	SH2X9	1.68	1.25	1.68E-06
27	SH2X10	0.65	0.14	6.50E-07
28	SH2X11	1.23	0.13	1.23E-06
29	SH2X12	1.60	0.14	1.60E-06

#	Sample Code	Lead concentration ug/g (ppm)	Standard Deviation	Percentage
30	SH2X15	1.21	0.26	1.21E-06
31	SH2X16	1.12	0.35	1.12E-06
32	SH2X17	1.22	0.31	1.22E-06
33	SH3X1	1.36	0.46	1.36E-06
34	SH3X2	2.12	0.27	2.12E-06
35	SH4	1.36	0.46	1.36E-06
36	SH5	3.48	0.44	3.48E-06
37	E1	0.63	0.26	6.28E-07
38	E3	1.14	0.15	1.14E-06
39	E4	1.76	0.38	1.76E-06
40	E5	5.97	1.60	5.97E-06
41	E6	17.08	6.93	1.71E-05
42	E7	0.97	0.84	9.73E-07
43	E8	2.83	0.40	2.83E-06
44	EB1X1	5.06	1.77	5.06E-06
45	EB1X2	1.88	0.65	1.88E-06
46	B2	3.84	3.04	3.84E-06
47	B3	1.67	0.43	1.67E-06
48	B4	2.06	0.41	2.06E-06
49	B5	6.85	3.29	6.85E-06
50	F1X1	1.73	0.32	1.73E-06
51	F1X2	2.07	0.62	2.07E-06
52	F1X3	1.56	1.01	1.56E-06
53	F2	1.42	0.35	1.42E-06
54	C1	2.09	2.61	2.09E-06
55	C2	2.60	2.93	2.60E-06
56	C3	2.78	1.81	2.78E-06
57	C4	1.89	2.27	1.89E-06
58	C5	3.42	4.43	3.42E-06
59	C6	1.41	1.50	1.41E-06
60	C7	1.57	0.00	1.57E-06
61	C8	1.34	0.40	1.34E-06

#	Sample Code	Lead concentration ug/g (ppm)	Standard Deviation	Percentage
62	C9	5.66	1.15	5.66E-06
63	C10	3.82	0.38	3.82E-06
64	C11X1	3.23	1.11	3.23E-06
65	C11X2	4.39	0.89	4.39E-06
66	C11X3	17.1	1.82	1.71E-05
67	C11X4	4.18	1.21	4.18E-06
68	L2	1.90	2.42	1.90E-06
69	L3	1.04	0.63	1.04E-06
70	L4	2.14	2.64	2.14E-06
71	L5	2.06	0.00	2.06E-06
72	L6	3.14	2.21	3.14E-06
73	L9	3758	720.95	3.76E-03
74	L10	0.81	0.54	8.05E-07
75	L11	1.83	0.76	1.83E-06
76	L12	1.00	0.22	9.98E-07
77	L15	3.28	0.65	3.28E-06
78	L16	3.36	0.82	3.36E-06
79	L17	19.09	4.15	1.91E-05
80	L18	6044	293	6.04E-03
81	L19	3.08	0.56	3.08E-06
82	L20	4.15	0.42	4.15E-06
83	L21	3.00	0.35	3.00E-06
84	L22	3.24	1.06	3.24E-06
85	L23	4.94	0.61	4.94E-06
86	L24	3.88	1.33	3.88E-06
87	L25	2.27	0.30	2.27E-06
88	L26	3.41	0.97	3.41E-06
89	L27	6.17	2.46	6.17E-06
90	NP1	1.20	0.68	1.20E-06
91	NP2	68.9	5.04	6.89E-05
92	NP3	1.52	0.41	1.52E-06
93	NP4	1.41	0.81	1.41E-06

#	Sample Code	Lead concentration ug/g (ppm)	Standard Deviation	Percentage
94	NP5	1.39	0.80	1.39E-06
95	NP6	0.97	0.48	9.73E-07
96	NP7	1.27	0.42	1.27E-06
97	NP8	1.10	0.63	1.10E-06
98	NP11	1.43	0.25	1.43E-06
99	NP12	1.48	0.85	1.48E-06
100	NP13	1.29	0.71	1.29E-06
101	NP14	1.50	0.71	1.50E-06
102	NP16	1.74	0.58	1.74E-06
103	NP17	5.55	1.05	5.55E-06
104	NP18	5.11	0.75	5.11E-06
105	NP19	7.11	1.89	7.11E-06
106	H1	7.45	1.20	7.45E-06
107	H1-2	6.41	0.17	6.41E-06
108	H1-3	3.14	1.08	3.14E-06
109	D1	1.73	1.08	1.73E-06
110	MS1	0.88	0.33	8.76E-07
111	MS2	3.28	0.94	3.28E-06
112	HR	1.29	0.74	1.29E-06
113	BC	0.81	0.17	8.13E-07

Table 4.2: Average Lead Concentration for Types of Cosmetics

Application	Pb concentration range (ppm)
Eyes	0.6 - 15
Lips	1.4 - 6044
Nails	0.7 -69
Face	1.0 - 17
Others	0.8 - 1.7

Table 4.3: Samples exceeding recommended maximum contaminant level of lead (Pb) according to US-FDA

Samples	Concentration (ppm)	Ratio to MCL
Eyeliner-6	17 ± 7.0	1.5
Concealer-11X3	17.1±1.8	1.7
Lipstick-17	19±4.2	1.9
Nail Polish-2	69±5.0	6.9
Lipstick-9	3758 ± 721	377
Lipstick-18	6044±293	605

Out of 140 samples tested, there are six samples exceeded the US.FDA limit for lead. The most toxics samples were lipsticks for the range 3037 to 6337 ppm of lead. These high concentrations indicate that lead exists as color additive. According to Bocca et al., lead oxides or lead chromate could be the sources of lead in these lipsticks as shown in **Table 4.4**.

Table 4.4: Possible lead Pb sources[1]

Lead Source	Possible Contaminated Samples
Lead oxide Pb_3O_4 (red)	Lipstick
Lead Chromate $PbCrO_4$ (yellow)	Lipsticks
Lead Carbonate $(PbCO_3)_2 \cdot Pb(OH)_2$ (white)	Nail polish
Ozokerite (Fossil wax after refining) yellow to white	Lipstick and mascara
Petrolatum	Facial creams
Galena PbS or Anglesite $PbSO_4$	Kohls

4.2. Rubidium (Rb) Concentrations in Cosmetics

The linearity of the method was good in the range 0.10-11 ppm, with a correlation coefficient of 0.9999. Also, the limit of detection for rubidium in MPAES is 1.75 ppb (*n*=20)

Table 4.5: Rubidium Concentrations in Cosmetics from MPAES

#	Sample Code	Rubidium Concentration ug/g (ppm)	Standard Deviation	Percentage
1	SH1X1	21.8	0.63	2.175E-05
2	SH1X2	11.3	0.29	1.130E-05
3	SH1X5	15.9	0.25	1.585E-05
4	SH1X6	25.0	0.66	2.496E-05
5	SH1X7	7.20	1.27	7.185E-06
6	SH1X8	5.60	0.16	5.610E-06
7	SH1X9	11.0	8.14	1.101E-05
8	SH1X10	12.7	0.24	1.274E-05
9	SH1X11	14.8	0.24	1.483E-05
10	SH1X12	13.1	0.22	1.306E-05
11	SH1X13	8.8	1.98	8.763E-06
12	SH1X14	17.4	0.22	1.735E-05
13	SH1X15	15.2	12.23	1.515E-05
14	SH1X16	18.2	2.14	1.820E-05
15	SH1X18	2.40	0.00	2.370E-06
16	B1X1	24.7	1.04	2.467E-05
17	B1X2	21.2	0.67	2.121E-05
18	SH2X1	10.1	0.17	1.015E-05
19	SH2X3	5.70	0.00	5.720E-06
20	SH2X4	8.60	0.38	8.620E-06
22	SH2X6	9.50	3.68	9.530E-06
23	SH2X7	9.20	0.33	9.230E-06
24	SH2X11	4.60	3.26	4.615E-06
25	SH2X12	3.50	0.17	3.480E-06
26	SH2X13	6.60	2.87	6.560E-06
27	SH2X14	3.60	0.48	3.587E-06
28	SH2X16	12.7	0.21	1.268E-05

#	Sample Code	Rubidium Concentration ug/g (ppm)	Standard Deviation	Percentage
29	SH2X17	13.6	0.59	1.357E-05
30	SH3X1	13.5	0.57	1.354E-05
31	SH3X2	7.30	0.79	7.253E-06
32	SH4	16.4	1.19	1.640E-05
33	SH5	6.4	0.55	6.420E-06
34	E3	11.8	0.00	1.178E-05
35	E4	11.1	0.33	1.106E-05
36	EB2	6.60	0.00	6.620E-06
37	B3	8.60	0.21	8.580E-06
38	B4	24.5	0.85	2.454E-05
39	B5	3.20	0.34	3.177E-06
40	L5	33.4	2.94	3.343E-05
41	L10	3.10	1.55	3.126E-06
42	H1	96.3	5.65	9.630E-05
43	H1-2	92.1	2.00	1.033E-04
44	H1-3	10.6	0.31	1.059E-05
46	Mica STD	6.80	0.00	6.750E-06

Therefore, the highest concentration of rubidium was in facial makeup which are highlighters, Highlighter1, Highlighter1-2, and Highlighter1-3. Next, Lipstick-5 has 33.4 ppm and eyeshadows comes in range 25 to 4 ppm of rubidium.

Table 4.6: Average Rubidium Results using MPAES

Application	Rubidium Concentration Range (ppm)
Eyes	3.6-25
Lips	3.1-33
Face	8.6-96

Table 4.7: Highlighter Samples and Their Rubidium Concentrations

Rubidium Positive Results	**Concentration (ppm)**
Highlighter-1	96±5.6
Highlighter-1-2	92±2.0
Highlighter1-3	11±0.3

Highlighter-1, Highlighter-1-2 and Highlighter-1-3 are all purportedly the same brand. However, Highlighter-1, Highlighter-1-2 are counterfeit products from unknown origin while Highlighter1-3 is original product purchased from USA market

According to the package labels, mica exist as an ingredient in these positive sample results, Rubidium exists in muscovite type of mica

CHAPTER V

MUSCOVITE AS A SOURCE OF LEAD IN COSMETICS

According to Finger and Schiller[31], muscovite can accumulate lead (Pb) up to 100 ppm in concentration. This suggested that mica could be the source of lead in those cosmetics that contacted this ingredient. The commercial mica used in this investigation was analyzed by MPAES and was found to contain 0.52 ppm of lead. While this is relatively low, it dose support the hypothesis that mica is a source of lead in cosmetics. To further investigate the relationship between lead and mica, the lead concentrations were plotted versus the rubidium concentration for the cosmetic samples.

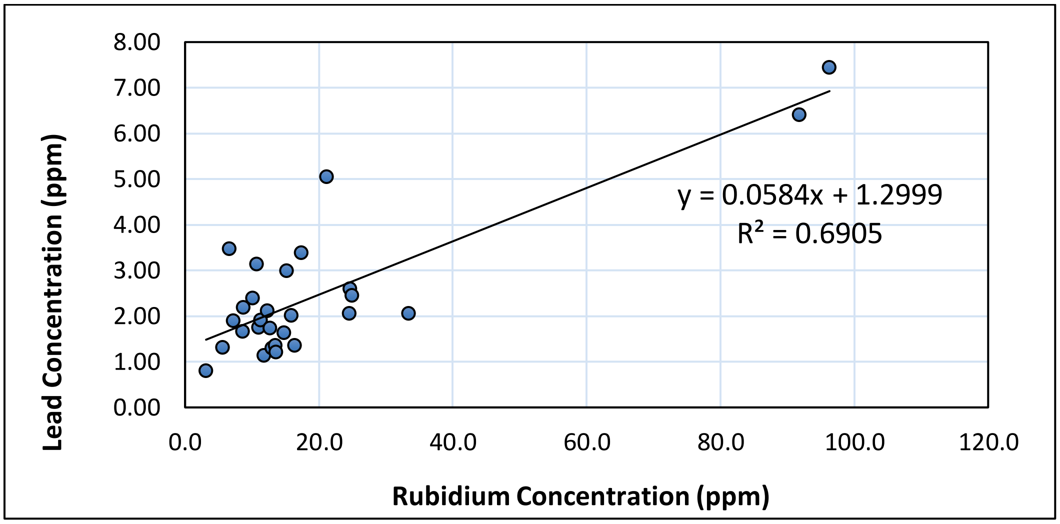

Figure 5.1: Linear Relationship Between Rubidium and Lead in Cosmetics that Contain Mica.

Hence, the rubidium concentration is used as an approximation for mica content although the rubidium content of muscovite is somewhat variable. A liner fit of the data gave a slope of 0.058 and r_2 of 0.69. Thus, the lead and rubidium (and thus mica) are correlated with each other. The r_2 is low since the micas likely come from different sources with varying amounts of lead and rubidium.

Another way of looking at this correlation, is to plot both the rubidium and lead concentration for each mica containing cosmetic sample for low lead concentration to high **Figure 5.2** This clearly shows that high concentrations occur with high rubidium concentrations.

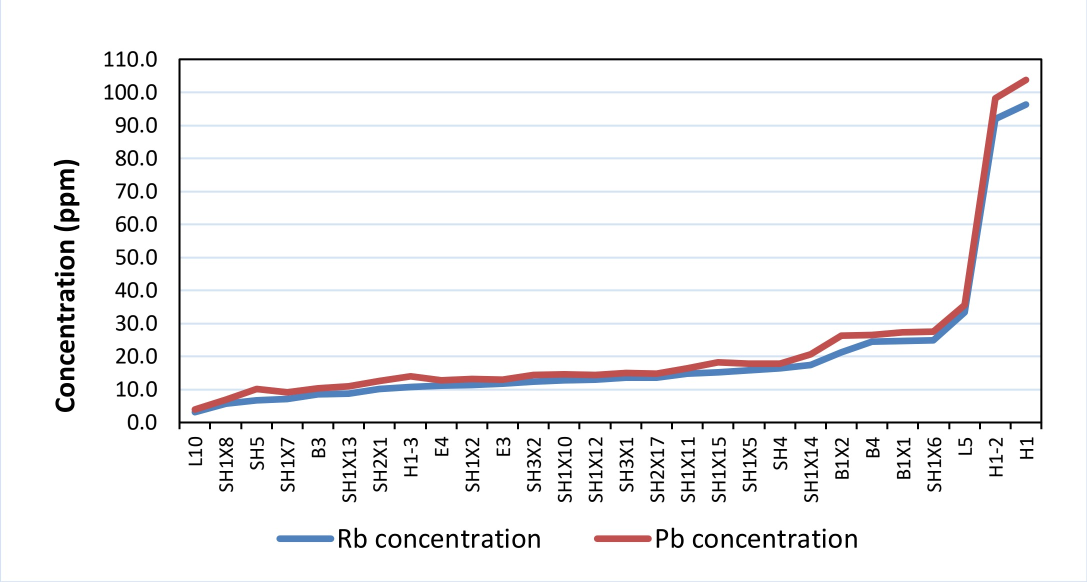

Figure 5.2: General Trend of Rubidium and Lead Correlation

CHAPTER VI

METHOD VALIDATION AND EVALUATIONS

6.1. Rubidium Results

Highlighter-1 package show it has mica in its ingredient. Therefore, X-ray diffraction done for the sample after extracted it with DCM and letting it dry to eliminate any impurities. Consequently, it matched muscovite type of mica which is rich of rubidium elements as shown in **Figure 6.1**

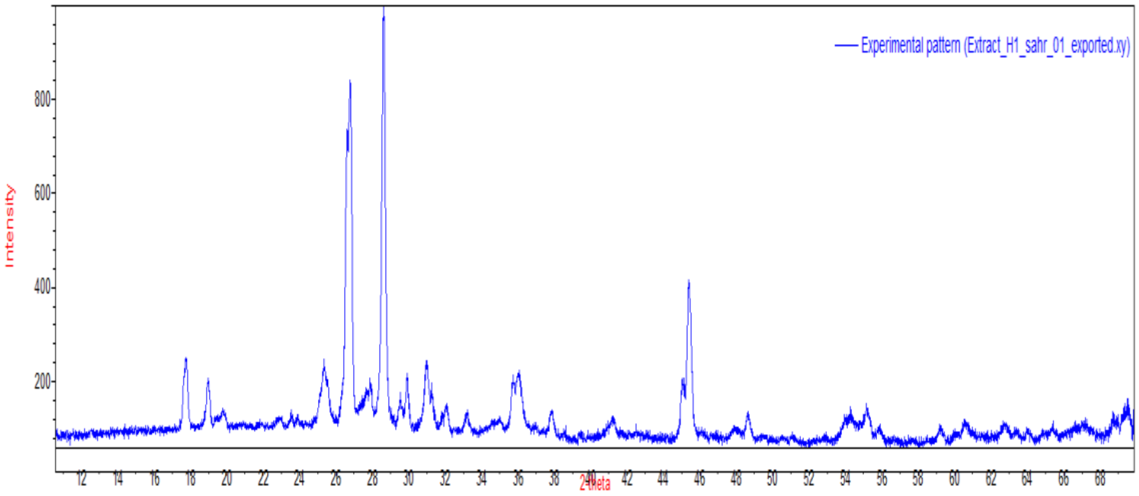

Figure 6.1: XRD Pattern for Highlighter-1

Figure 6.2: Commercial Muscovite **Figure 6.3:** Highlighter-1

A comparison of the infrared spectra of both muscovite and highlighter-1 sample before and after extraction of the organics with dichloromethane is shown in **Figure 6.4** Therefore, it approves the agreement of having matching fingerprints of mica peaks of infrared between 500-1000 cm-1.

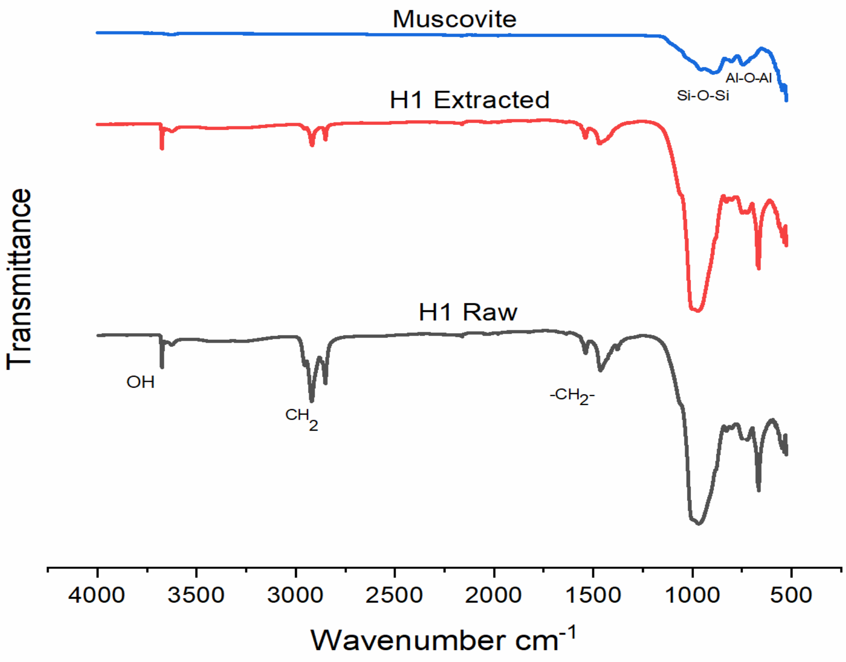

Figure 6.4: Infrared spectra of muscovite and highlighter 1

The common broad peaks between 500 and 1000 cm^{-1} supports the presence of mica in highlighter-1

6.2. Lead Results

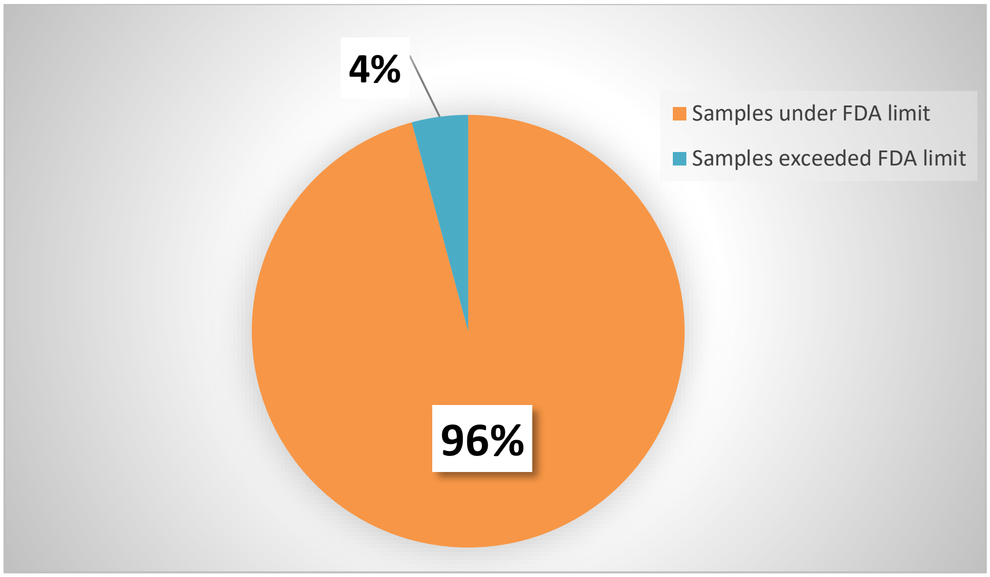

Figure 6.5: Percentage of Tested Cosmetic Samples Violated FDA Permissional Limit

6.2.1 Samples Exceeding Recommended Maximum Contaminant Level of Lead (Pb)

There are six samples that exceeded the FDA limit of10 ppm by factor of 1.5-605 times, the concentrations ranged from 17 ± 7.0 ppm to 6044±293 ppm. The highest lead concentration was in lipstick-18 **Figure 6.6**.

1- Lipstick-18

Figure 6.6: Lipstick-18

Lipstick-18 has an extremely high concentration of lead Pb 6044±293 mg/kg. For this reason, this sample was further investigated by X-ray fluorescence XRF, X-ray diffraction XRD and Infrared IR to identify the lead compound present.

In addition, there are several intense peaks of other elements such as silicon Si, calcium Ca, titanium Ti, Chromium Cr, and iron Fe. The very intense peak was Ti for about 5.10E+07±1.81E+05 counts while chromium is 5.26E+06±1.89E+04 counts.

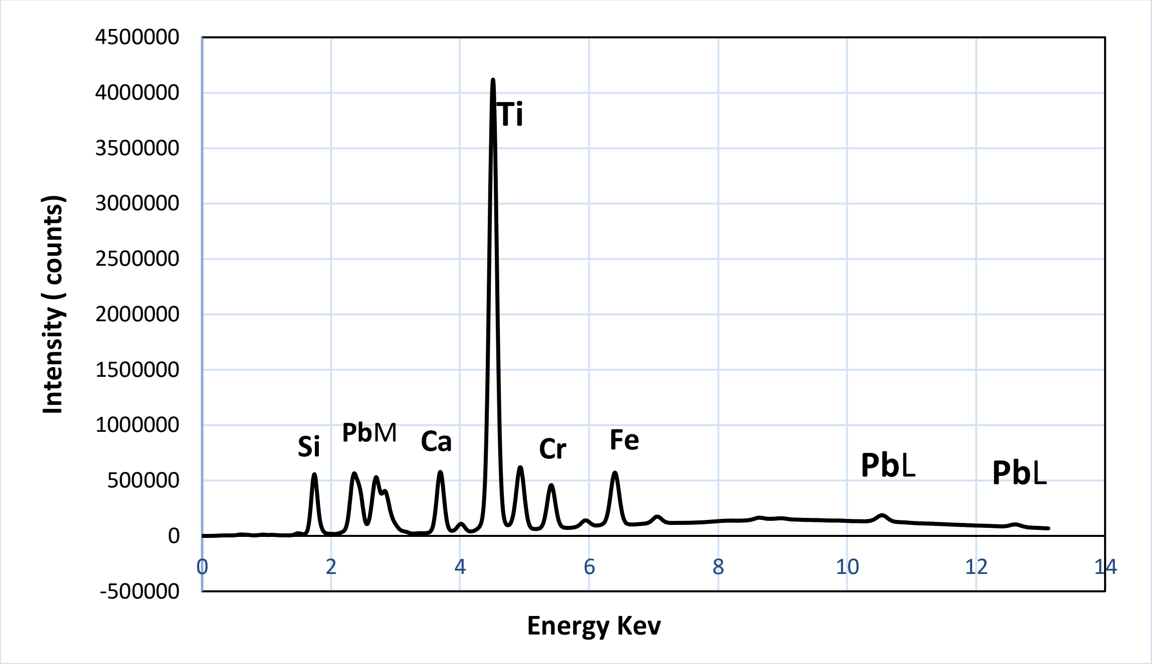

Figure 6.7: X-ray fluorescence spectrum of Lipstick-18

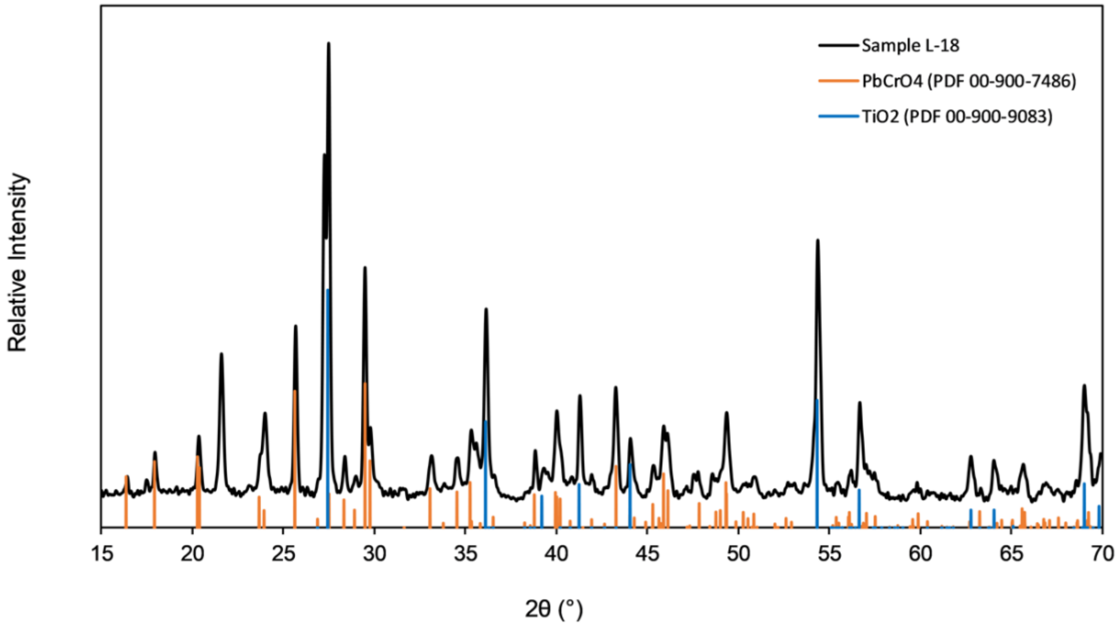

Figure 6.8: X-Ray Diffraction Pattern of Lipstick-18

Since the sample made of several inorganic colorants, XRD showed match with lead chromate $PbCrO_4$ and rutile TiO_2 at the same time, also the physical appearance of Lead (II) chromate after extraction by dichloromethane as clear yellow liquid which confirm that Lead (II) chromate is the source of lead in lipstick-18.

Figure 6.9: Extraction Separation of Lipstick-18 using Dichloromethane

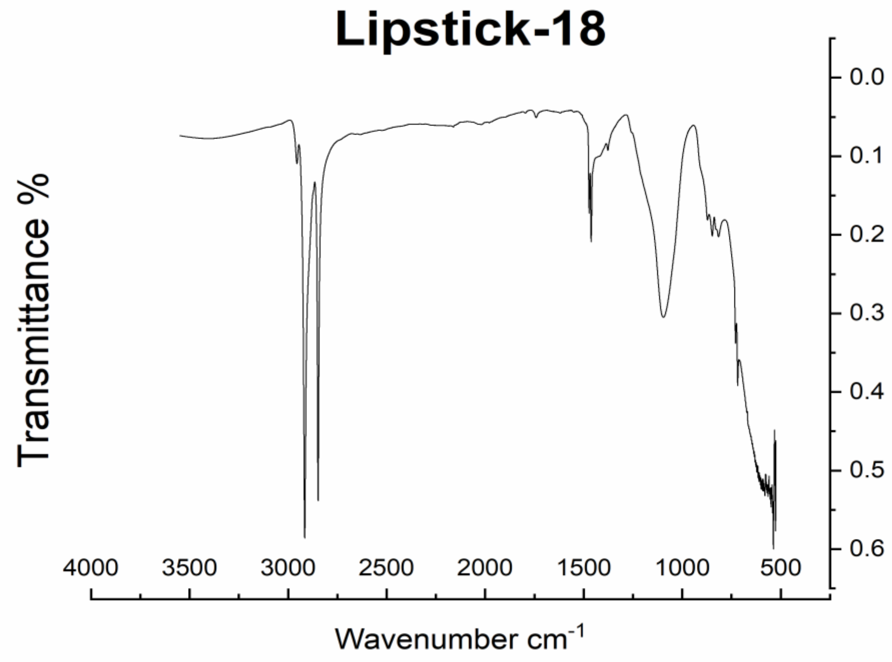

Figure 6.10: Infrared Spectrum of Lipstick-18

An infrared spectra for that sample where it shows chromate CrO_4^{-2} peak appeared at 873 cm^{-1} , in addition to peaks at 1712 cm^{-1} for C=O stretch, 2848 cm^{-1} and 2916 cm^{-1} for C-H. Moreover, this sample contains rutile TiO_2 and that can be shown from peak 591 where it represents Ti-O stretch

Therefore, Fe_2O_3, TiO_2[32] and $PbCrO_4$ used as colorants, also rutile has been used in cosmetics as sunscreen, where it has ability to minimize UV light exposure on skin[33] Ingestion and inhalation of chromate can cause neurotoxicity and carcinogenic[34]. Not only lead is toxic in this compound but also chromate contains Cr(VI), which penetrate the red blood cells, are reduced from $Cr^{6+} \rightarrow Cr^{3+}$ that bound to hemoglobin, resulting in a stable tagging of the red blood cells[35]

2- Lipstick-9

It has the second highest concentration of lead for about 3758 ± 721 mg/kg. It could have lead tetroxide Pb_3O_4 because of its red color.

Figure 6.12: Lipstick-9

The lead concentration found about 3758 ± 721 ppm, which is about 400 times higher than the permitted limit

3- Nail Polish-2

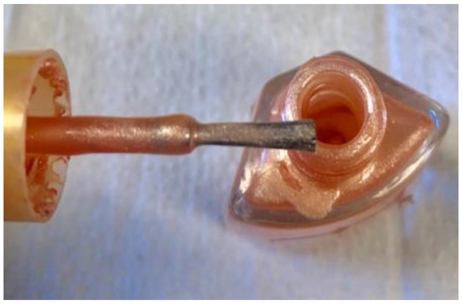

Figure 6.13: Nail Polish 2

The lead concentration in this nail polish is about 70 ppm.

4- **Lipstick-17**

Figure 6.14: Lipstick-17

The lead concentration found in this dark liquid lipstick about 19±4.2 via MPAES

5- **Concealer-11X3**

Figure 6.15: Concealer-11X3

Concealer11-X3 has pale purple color and it is typically used for opposing yellow undertones of skin and brighten the face spots discoloration. The lead concentration found about 17.0±1.81 via MPAES.

6.3. Molybdenum Hair Dye-1

Hair Dye-1 is black hair powder dye. Its XRF spectrum shows that it has very high intensity of molybdenum and sulfur that overlap each other at the region 200-300 kV indicate the presence of MoS_2

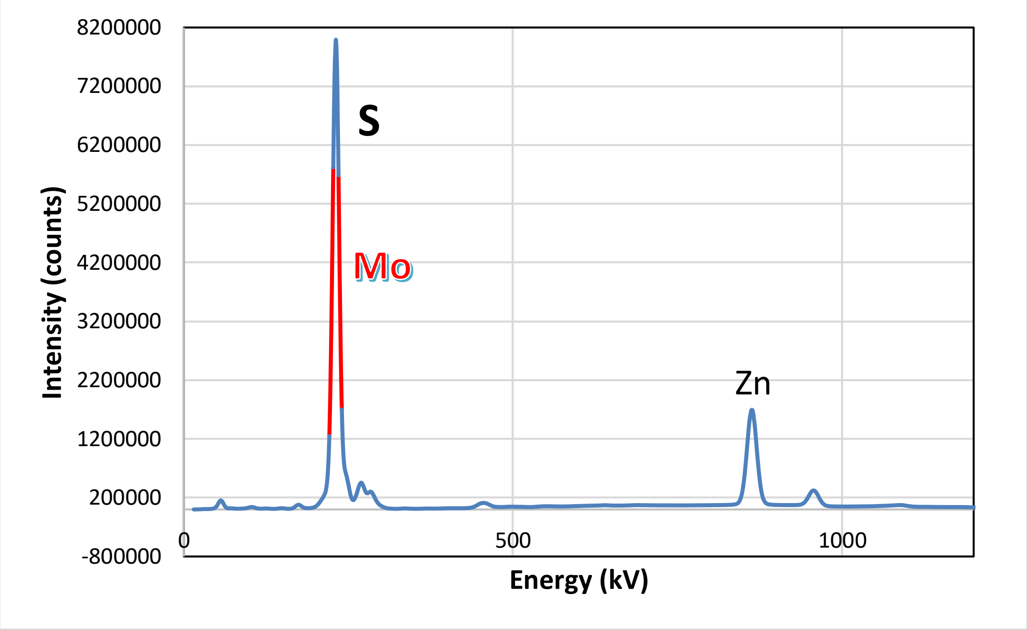

Figure 6.16: X-Ray Fluorescence Spectrum for Hair Dye-1

6.4. Comparison Between MPAES and XRF of Lead and Rubidium Results

A compassion study and evaluation done between microwave plasma atomic emission and X-ray fluorescence spectroscopy results in measuring the same element concentration in the same sample. However, the difference was XRF measured the sample in its raw material without any treatment.

Table 6.1: Samples Contain Rubidium Results

Samples	XRF (ppm)	MPAES (ppm)
SH5	8.9±0.7	6.7±0.5
E3	14±0.5	12±0.0
SH1X5	45±0.6	16±0.2
B1X2	61±1.8	21±0.6

However, other calibration curves gave varied results as shown in table

Table 6.2: Variation in Rubidium Results among different instruments and different standard types.

	XRF via Mica Standards	**XRF via Rb-Silica Standards**	**MP-AES**
Sample Codes	**Rb Concentration (ppm)**	**Rb Concentration (ppm)**	**MP Rubidium (ppm)**
SH1X5	44.9	137	15.9
SH1X13	21.1	111	8.80
SH1X16	44.6	136	18.2
SH1X18	628	764	2.40
B1X2	61.3	154	21.2
SH2X4	49.0	141	8.60
SH2X6	51.3	144	9.50
SH2X12	8.10	96.8	3.50
SH2X13	184	286	6.60
SH2X14	653	791	3.60
SH3X2	8.00	96.8	7.30
E5	391	509	6.40
EB2	223	329	6.60
L5	144	244	33.4

Table 6.3: Samples Contain Lead Pb Results

#	Sample Code	XRF (ppm)	MPAES (ppm)
1	SH1X1	Below LOD	1.9
2	SH1X2	0.4	1.9
3	SH1X3	1.3	1.4
4	SH1X4	Below LOD	Below LOD
5	SH1X5	0.4	2.0
6	SH1X6	0.6	2.5
7	SH1X7	0.3	1.9
8	SH1X8	0.3	1.3
9	SH1X9	0.2	Below LOD
10	SH1X10	0.5	1.7
11	SH1X11	0.4	1.6
12	SH1X12	1.1	1.3
13	SH1X13	0.5	2.2
14	SH1X14	0.5	3.4
15	SH1X15	0.8	3.0
16	SH1X16	1.0	Below LOD
17	SH1X17	0.2	7.8
18	SH1X18	1.6	2.5
19	B1X1	3.5	2.6
20	B1X2	1.0	5.1
21	L1X1	0.7	0.7
22	L1X2	0.7	2.3
23	L1X3	0.5	0.9
24	L1X4	0.6	2.7
25	L1X5	0.4	0.7
26	L1X6	0.4	0.5
27	L1X7	0.3	0.4
28	L1X8	0.5	0.2
29	L1X9	Below LOD	0.4
30	L1X10	Below LOD	Below LOD
31	L1X11	Below LOD	0.7
32	L1X12	Below LOD	0.5
33	SH2X1	0.7	2.4
34	SH2X2	0.1	Below LOD
35	SH2X3	0.2	2.5

#	Sample Code	XRF (ppm)	MPAES (ppm)
36	SH2X4	2.1	1.8
37	SH2X5	1.9	1.4
38	SH2X6	1.9	1.9
39	SH2X7	0.4	Below LOD
40	SH2X8	5.3	1.2
41	SH2X9	0.2	1.7
42	SH2X10	3.9	0.7
43	SH2X11	2.3	1.2
44	SH2X12	1.7	1.6
45	SH2X13	5.8	Below LOD
46	SH2X14	3.2	Below LOD
47	SH2X15	1.4	1.2
48	SH2X16	2.3	1.1
49	SH2X17	1.0	1.2
50	SH3X1	1.2	1.4
51	SH3X2	5.1	2.1
52	SH4	1.0	1.4
53	SH5	3.8	3.5
54	E1	0.1	0.6
55	E2	0.2	Below LOD
56	E3	0.9	1.1
57	E4	0.7	1.8
58	E5	1.5	6.0
59	E6	1.5	17.1
60	E7	0.5	1.0
61	E8	0.3	2.8
62	EB1X1	0.8	5.1
63	EB1X2	8.3	1.9
64	EB2	0.5	Below LOD
65	B2	0.5	3.8
66	B3	1.2	1.7
67	B4	0.8	2.1
68	B5	1.3	6.9
69	F1X1	3.6	1.7
70	F1X2	2.2	2.1
71	F1X3	1.2	1.6
72	F2	10	1.4
73	C1	Below LOD	2.1

#	Sample Code	XRF (ppm)	MPAES (ppm)
74	C2	2.6	2.6
75	C3	0.2	2.8
76	C4	0.2	1.9
77	C5	7.5	3.4
78	C6	0.3	1.4
79	C7	2.5	1.6
80	C8	0.1	1.3
81	C9	10	5.7
82	C10	11	3.8
83	C11X1	3.0	3.2
84	C11X2	2.3	4.4
85	C11X3	0.3	17
86	C11X4	5.7	4.2
87	L2	0.3	1.9
88	L3	Below LOD	1.0
89	L4	24	2.1
90	L5	6.4	2.1
91	L6	0.2	3.1
92	L7	1.7	3.8
93	L8	5.7	Below LOD
94	L9	5352	3758
95	L10	2.5	0.8
96	L11	3.6	1.8
97	L12	0.2	1.0
98	L13	0.4	Below LOD
99	L14	1.0	Below LOD
100	L15	0.4	3.3
101	L16	1.0	3.4
102	L17	Below LOD	19
103	L18	6554	6044
104	L19	0.6	3.1
105	L20	Below LOD	4.2
106	L21	0.1	3.0
107	L22	0.2	3.2
108	L23	0.1	4.9
109	L24	0.4	3.9
110	L25	3.2	2.3
111	L26	3.5	3.4

#	Sample Code	XRF (ppm)	MPAES (ppm)
112	L27	4.7	6.2
113	NP1	0.1	1.2
114	NP2	1.4	69
115	NP3	Below LOD	1.5
116	NP4	0.2	1.4
117	NP5	0.6	1.4
118	NP6	0.1	1.0
119	NP7	0.3	1.3
120	NP8	Below LOD	1.1
121	NP11	0.2	1.4
122	NP12	1.0	1.5
123	NP13	0.2	1.3
124	NP14	0.7	1.5
125	NP15	Below LOD	Below LOD
126	NP16	1.1	1.7
127	NP17	0.1	5.5
128	NP18	Below LOD	5.1
129	NP19	0.3	7.1
130	H1	1.1	7.4
131	H1-2	1.3	6.4
132	H1-3	3.7	3.1
133	D1	4.2	1.7
134	LO1	1.2	Below LOD
135	MS1	0.4	0.9
136	MS2	1.1	3.3
137	HR	0.2	1.3
138	BC	0.3	0.8

As a result, the results between the two instruments reasonably near to each other. Therefore, XRF made excellent conclusion that it can be sensitive and selective as much as AES

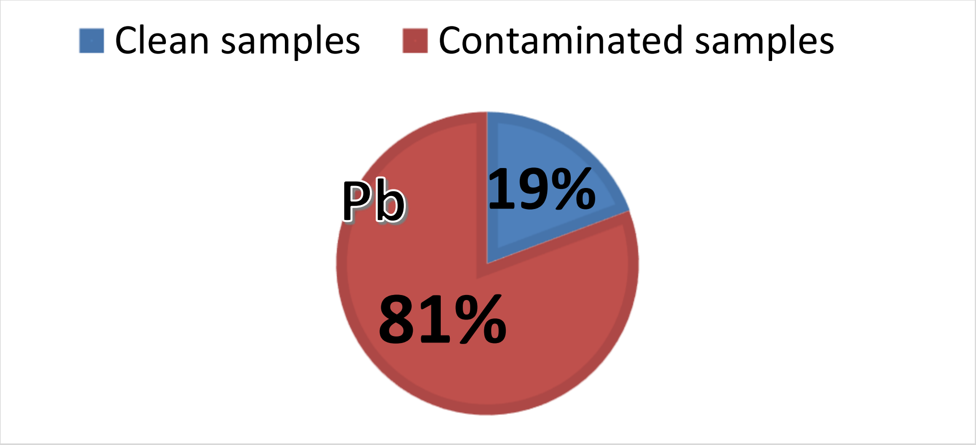

Figure 6.17: Percentage of Pb Contaminated Cosmetic Samples Tested

A study states that consumers ingest about 4 to 9 pounds of lipstick on average over their lifetime[36] Therefore, lipsticks should be re-regulated for lead levels, or its use should be banned as countries of the European Union (EU) have decided.

At least, it should be recommended to treat lipsticks as candies when manufacturing them and they should not exceed 0.1 ppm lead[37].

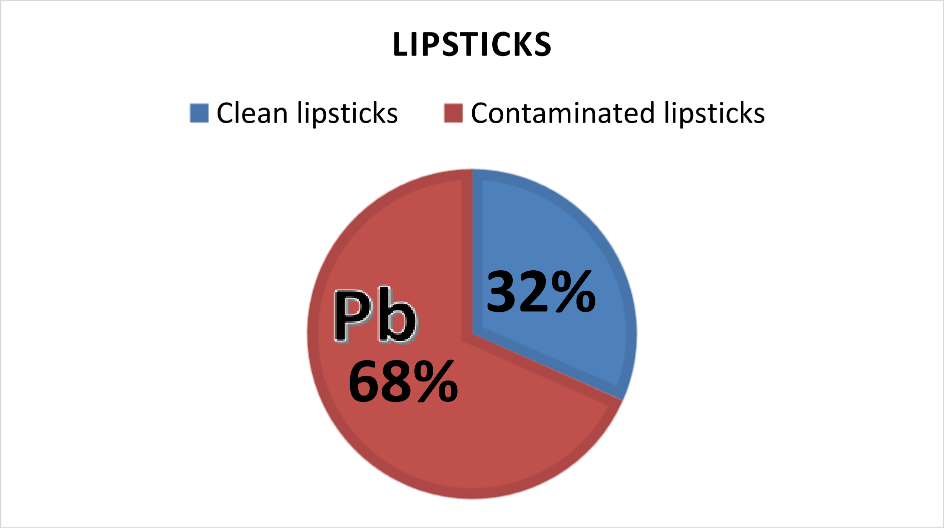

Figure 6.18: Percentage of Contaminated Lipstick Samples Tested

The contaminated products that exceeded the FDA maximum contaminant level are from China. However, all US made samples were below the limit. Most positive results violated not only US good manufacturing practices but also did not obey the countries legislations, such as Canada and the EU[1.] This project identified high concentrations and intensities of some elements and what are their sources. Approved correlation between Pb and mica, and this conclude that mica can be unintentional reason for Pb existence in most cosmetic samples. Mica should be cleaned before manufacturing cosmetic products. Limit of detection for Pb in XRF provides best way to screen lead in cosmetics according to the FDA standards.

6.5. Conclusion

To compare X-Ray Fluorescence to Microwave Plasma Atomic Emission Spectroscopy, XRF is a non-destructive, cost-effective and time-saving method compared to MPAES or any AES. Normally, concentrations are obtained in few seconds up to minutes. Moreover, this type of analysis does not require any pre-sample treatment that conserve the analyzed sample without causing any damage. On the other hand, AES techniques require for the most part a sample preparation that irreversibly changes the sample initial state. The comparison results in linear regression and the determination of the correlation coefficient making it possible to consider the correlation between these two methods and thus the quality of the measurements made by the XRF.

CHAPTER VII

SUMMARY AND CONCLUSION

A study states that consumers ingest about 4 to 9 pounds of lipstick on average over their lifetime,[36] therefore, lipsticks should be re-regulated for lead levels, or its use should be banned as countries of the European Union (EU) have decided. Or at least, it should be recommended to treat lipsticks as candies when manufacturing them and they should not exceed 0.1 ppm lead.[37]

Finally, this study addresses the necessity to look deeper at safety, health and security statutes. Using daily products become unsafe and could be toxic and deadly in long term for consumers. Not only consumers affected but also manufacture labor, too. One of the safety, security, health and environmental element is plant management[38] where risk control taking place to ensure commissioning, storage , transportation , maintenance and disposal are applied correctly and avoid any possible contaminations. Moreover, cosmetic suppliers should have responsibility on importing merchandise that are not safe or toxic. According to Tomma[38], the suppliers have two duties, first one, substance must be safe, second one, should not have any type of risk using this substance. For instance, mica cosmetics should not be as loose powder, but at least be pressed to minimize the effect of flying particles which consequently will harm through breathing.

REFERENCES

1. Bocca, B.; Pino, A.; Alimonti, A.; Forte, G., Toxic metals contained in cosmetics: a status report. *Regul Toxicol Pharmacol* **2014,** *68* (3), 447-67.
2. Bilal, M.; Iqbal, H. M. N., An insight into toxicity and human-health-related adverse consequences of cosmeceuticals - A review. *Sci Total Environ* **2019,** *670*, 555-568.
3. S K Chaudhri, N. K. J., History of cosmetics. *Asian Journal of Pharmaceutics* **2009**, 164-167.
4. Lucas, A., Cosmetics, Perfumes and Incense in Ancient Egypt. *The Journal of Egyptian Archaeology* **1930,** *16* (1/2), 41-53.
5. Allen, J. P.; Mininberg, D. T., *The art of medicine in ancient Egypt*. Metropolitan Museum of Art: 2005.
6. Berry, S., *Screen style: Fashion and femininity in 1930s Hollywood*. U of Minnesota Press: 2000.
7. Safe Cosmetics. *The British Medical Journal* **1961,** *2* (5268), 1697-1697.
8. Hazards From Cosmetics And Toilet Preparations. *The British Medical Journal* **1961,** *2* (5268), 1700-1701.
9. Liang, B. A.; Hartman, K. M., It's only skin deep: FDA regulation of skin care cosmetics claims. *Cornell J Law Public Policy* **1999,** *8* (2), 249-80.
10. Millikan, L. E., Cosmetology, cosmetics, cosmeceuticals: definitions and regulations. *Clin Dermatol* **2001,** *19* (4), 371-4.
11. FDA's Testing of Cosmetics for Arsenic, Cadmium, Chromium, Cobalt, Lead, Mercury, and Nickel Content. https://www.fda.gov/cosmetics/potential-contaminants-cosmetics/fdas-testing-cosmetics-arsenic-cadmium-chromium-cobalt-lead-mercury-and-nickel-content (accessed 09/30/2019).
12. Bowman, D. M.; van Calster, G.; Friedrichs, S., Nanomaterials and regulation of cosmetics. *Nature Nanotechnology* **2010,** *5* (2), 92-92.
13. Clarke, L. H.; Bundon, A., From 'the thing to do' to 'defying the ravages of age': older women reflect on the use of lipstick. *J Women Aging* **2009,** *21* (3), 198-212.
14. Al-Saleh, I.; Al-Enazi, S.; Shinwari, N., Assessment of lead in cosmetic products. *Regul Toxicol Pharmacol* **2009,** *54* (2), 105-13.
15. Hepp, N. M.; Mindak, W. R.; Cheng, J., Determination of total lead in lipstick: development and validation of a microwave-assisted digestion, inductively coupled plasma-mass spectrometric method. *J Cosmet Sci* **2009,** *60* (4), 405-14.
16. Parry, C.; Eaton, J., Kohl: a lead-hazardous eye makeup from the Third World to the First World. *Environmental health perspectives* **1991,** *94*, 121-123.

17. Volpe, M.; Nazzaro, M.; Coppola, R.; Rapuano, F.; Aquino, R., Determination and assessments of selected heavy metals in eye shadow cosmetics from China, Italy, and USA. *Microchemical Journal* **2012,** *101*, 65-69.
18. Nnorom, I.; Igwe, J.; Oji-Nnorom, C., Trace metal contents of facial (make-up) cosmetics commonly used in Nigeria. *African Journal of Biotechnology* **2005,** *4* (10).

1. Bocca, B.; Pino, A.; Alimonti, A.; Forte, G., Toxic metals contained in cosmetics: a status report. *Regul Toxicol Pharmacol* **2014,** *68* (3), 447-67.
2. Bilal, M.; Iqbal, H. M. N., An insight into toxicity and human-health-related adverse consequences of cosmeceuticals - A review. *Sci Total Environ* **2019,** *670*, 555-568.
3. S K Chaudhri, N. K. J., History of cosmetics. *Asian Journal of Pharmaceutics* **2009**, 164-167.
4. Lucas, A., Cosmetics, Perfumes and Incense in Ancient Egypt. *The Journal of Egyptian Archaeology* **1930,** *16* (1/2), 41-53.
5. Allen, J. P.; Mininberg, D. T., *The art of medicine in ancient Egypt*. Metropolitan Museum of Art: 2005.
6. Berry, S., *Screen style: Fashion and femininity in 1930s Hollywood*. U of Minnesota Press: 2000.
7. Safe Cosmetics. *The British Medical Journal* **1961,** *2* (5268), 1697-1697.
8. Hazards From Cosmetics And Toilet Preparations. *The British Medical Journal* **1961,** *2* (5268), 1700-1701.
9. Liang, B. A.; Hartman, K. M., It's only skin deep: FDA regulation of skin care cosmetics claims. *Cornell J Law Public Policy* **1999,** *8* (2), 249-80.
10. Millikan, L. E., Cosmetology, cosmetics, cosmeceuticals: definitions and regulations. *Clin Dermatol* **2001,** *19* (4), 371-4.
11. FDA's Testing of Cosmetics for Arsenic, Cadmium, Chromium, Cobalt, Lead, Mercury, and Nickel Content. https://www.fda.gov/cosmetics/potential-contaminants-cosmetics/fdas-testing-cosmetics-arsenic-cadmium-chromium-cobalt-lead-mercury-and-nickel-content (accessed 09/30/2019).
12. Bowman, D. M.; van Calster, G.; Friedrichs, S., Nanomaterials and regulation of cosmetics. *Nature Nanotechnology* **2010,** *5* (2), 92-92.
13. Clarke, L. H.; Bundon, A., From 'the thing to do' to 'defying the ravages of age': older women reflect on the use of lipstick. *J Women Aging* **2009,** *21* (3), 198-212.
14. Al-Saleh, I.; Al-Enazi, S.; Shinwari, N., Assessment of lead in cosmetic products. *Regul Toxicol Pharmacol* **2009,** *54* (2), 105-13.
15. Hepp, N. M.; Mindak, W. R.; Cheng, J., Determination of total lead in lipstick: development and validation of a microwave-assisted digestion, inductively coupled plasma-mass spectrometric method. *J Cosmet Sci* **2009,** *60* (4), 405-14.
16. Parry, C.; Eaton, J., Kohl: a lead-hazardous eye makeup from the Third World to the First World. *Environmental health perspectives* **1991,** *94*, 121-123.
17. Volpe, M.; Nazzaro, M.; Coppola, R.; Rapuano, F.; Aquino, R., Determination and assessments of selected heavy metals in eye shadow cosmetics from China, Italy, and USA. *Microchemical Journal* **2012,** *101*, 65-69.

18. Nnorom, I.; Igwe, J.; Oji-Nnorom, C., Trace metal contents of facial (make-up) cosmetics commonly used in Nigeria. *African Journal of Biotechnology* **2005,** *4* (10).
19. Brandao, J.; Okonkwo, O.; Sehkula, M.; Raseleka, R., Concentrations of lead in cosmetics commonly used in South Africa. *Toxicological & Environmental Chemistry* **2012,** *94* (1), 70-77.
20. AI-Saleh, I. A.; Coate, L., Lead exposure in Saudi Arabia from the use of traditional cosmetics and medical remedies. *Environmental Geochemistry and Health* **1995,** *17* (1), 29-31.
21. Lekouch, N.; Sedki, A.; Nejmeddine, A.; Gamon, S., Lead and traditional Moroccan pharmacopoeia. *Science of the Total Environment* **2001,** *280* (1-3), 39-43.
22. Kanias, G. D., Determination of trace elements in eyeshadow face powder and rouge make-up cosmetics by neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry* **1985,** *89* (2), 487-496.
23. Emad A. M. Farrag, M. H. E. A. S. l., Mohammed I. Abu Al-Sayyed, Study of heavy metals concentration in cosmetics purchased from Jordan markets by ICP-MS and ICP-OES. *International Journal of the Bioflux Society* **2015**.
24. www.marieclaire.com, Vol. 480X719.
25. Muscovite. mindat.org: 2006.
26. What's In My Products. https://www.cosmeticsinfo.org/whats-my-products?ingredient_id=607.
27. Hazardous Substance Fact Sheet of Mica. In *1659*, Services, N. J. D. o. H. a. S., Ed. NEW JERSEY DEPARTMENT OF HEALTH AND SENIOR SERVICES: 1996.
28. Tan, X.; Wang, Z.; Wang, Z., A Facile Acidic Digestion Method for Cosmetic Lead and Cadmium Determination by an Inductively Coupled Plasma Atomic Emission Spectrometer. *Journal of Applied Spectroscopy* **2018,** *85* (4), 659-664.
29. Zachariadis, G. A.; Sahanidou, E., Multi-element method for determination of trace elements in sunscreens by ICP-AES. *J Pharm Biomed Anal* **2009,** *50* (3), 342-8.
30. Gooch, J. W., *Lead-based paint handbook*. New York : Plenum Press: New York, 1993.
31. Finger, F.; Schiller, D., Lead contents of S-type granites and their petrogenetic significance. *Contributions to Mineralogy and Petrology* **2012,** *164* (5), 747-755.
32. Zhang, H.; Dong, Z. Preparation of colored rutile type titania nanoparticle used in cosmetics. CN102018630A, 2011.
33. Zhang, X.; Zhang, B.; Sun, B. Superfine ultraviolet-resistant rutile titanium dioxide for cosmetic and its preparation method. CN108410214A, 2018.
34. Lead Chromate. 2016-10-25 ed.; National Library of Medicine HSDB Database: toxnet, Toxicology Data Network.
35. Devoy, J.; Géhin, A.; Müller, S.; Melczer, M.; Remy, A.; Antoine, G.; Sponne, I., Evaluation of chromium in red blood cells as an indicator of exposure to hexavalent chromium: An in vitro study. *Toxicology Letters* **2016,** *255*, 63-70.
36. DID YOU KNOW WOMEN EAT 9 LBS OF LIPSTICK IN A LIFETIME? https://www.beautybakerie.com/blogs/ice-cream-social/why-wearing-beauty-bakerie-will-prevent-you-from-eating-9-pounds-of-lipstick (accessed 4/9/2019).
37. Guidance for Industry: Lead in Candy Likely To Be Consumed Frequently by Small Children. https://www.fda.gov/Food/GuidanceRegulation/GuidanceDocumentsRegulatoryInformati

on/ChemicalContaminantsMetalsNaturalToxinsPesticides/ucm077904.htm (accessed 4/5/2019).
38. Tooma, M., *Safety, Security, Health and Environment Law*. 1 ed.; The Frederation Press: 2008.

APPENDICES

Sample Codes:

- SH: eyeshadow
- E: eyeliner
- EB: eyebrow
- MS: mascara
- L: lipstick
- NP: nail polish
- B: blusher
- H: highlighter
- C: facial cream
- F: facial foundation
- D: Hair dye
- LO: body lotion
- HR: henna
- BC: body cream

Sample Lab Code	Brand Origin and Packaging Label	Sample's Color Number & Appearance
SH1X1	(Taiwan Origin) Color Treats, Groovy Compacts	Shimmery Lilac, Pressed Powder
SH1X2	(Taiwan Origin) Color Treats, Groovy Compacts	Matte Orange, Pressed Powder
SH1X3	(Taiwan Origin) Color Treats, Groovy Compacts	Creamy White, Pressed Powder
SH1X4	(Taiwan Origin) Color Treats, Groovy Compacts	Matte Black, Pressed Powder
SH1X5	(Taiwan Origin) Color Treats, Groovy Compacts	Matte Light Pink, Pressed Powder
SH1X6	(Taiwan Origin) Color Treats, Groovy Compacts	Pale Yellow, Pressed Powder
SH1X7	(Taiwan Origin) Color Treats, Groovy Compacts	Apple Green, Pressed Powder
SH1X8	(Taiwan Origin) Color Treats, Groovy Compacts	Shimmery Hot Pink, Pressed powder
SH1X9	(Taiwan Origin) Color Treats, Groovy Compacts	Cranberry, Pressed powder
SH1X10	(Taiwan Origin) Color Treats, Groovy Compacts	Lime, Pressed Powder
SH1X11	(Taiwan Origin) Color Treats, Groovy Compacts	Emerald, Pressed Powder
SH1X12	(Taiwan Origin) Color Treats, Groovy Compacts	Orange, Pressed Powder
SH1X13	(Taiwan Origin) Color Treats, Groovy Compacts	Metallic eggplant, Pressed Powder
SH1X14	(Taiwan Origin) Color Treats, Groovy Compacts	Blue, Pressed Powder
SH1X15	(Taiwan Origin) Color Treats, Groovy Compacts	Scarlet, Pressed Powder
SH1X16	(Taiwan Origin) Color Treats, Groovy Compacts	Plum, Pressed Powder
SH1X17	(Taiwan Origin) Color Treats, Groovy Compacts	Black, Pressed Powder
SH1X18	(Taiwan Origin) Color Treats, Groovy Compacts	Matte Brown, Pressed Powder
B1X1	(Taiwan Origin) Color Treats, Groovy Compacts	Beige, Pressed Powder (bronzer)
B1X2	(Taiwan Origin) Color Treats, Groovy Compacts	Brick, Pressed Powder (blusher)
L1X1	(Taiwan Origin) Color Treats, Groovy Compacts	Rust, Soft Lip Color
L1X2	(Taiwan Origin) Color Treats, Groovy Compacts	Beige, Soft Lip Cream
L1X3	(Taiwan Origin) Color Treats, Groovy Compacts	Orange, Soft Lip Cream
L1X4	(Taiwan Origin) Color Treats, Groovy Compacts	Indian Red, Soft Lip Cream
L1X5	(Taiwan Origin) Color Treats, Groovy Compacts	Coral, Soft Lip Cream
L1X6	(Taiwan Origin) Color Treats, Groovy Compacts	Ivory, Soft Lip Cream
L1X7	(Taiwan Origin) Color Treats, Groovy Compacts	Imperial, Soft Lip Cream
L1X8	(Taiwan Origin) Color Treats, Groovy Compacts	Metallic Mauve, Soft Lip Cream
L1X9	(Taiwan Origin) Color Treats, Groovy Compacts	Light Pink, Soft Lip Cream
L1X10	(Taiwan Origin) Color Treats, Groovy Compacts	Mulberry, Soft Lip Cream
L1X11	(Taiwan Origin) Color Treats, Groovy Compacts	Metallic Thulian, Soft Lip Cream
L1X12	(Taiwan Origin) Color Treats, Groovy Compacts	Metallic Brown, Soft Lip Cream
SH2X1	(US Origin) Eyeshadow	Pressed Powder, Blue
SH2X2	(US Origin) Makeup Kit	Pressed Powder, Matte Light Brown (Bronzer)
SH2X3	(US Origin) Makeup Kit	Pressed Powder, White
SH2X4	(US Origin) Makeup Kit	Pressed Powder, Metallic Dark Brown
SH2X5	(US Origin) Makeup Kit	Pressed Powder, Metallic Brown
SH2X6	(US Origin) Makeup Kit	Pressed Powder, Shimmery Camel

Sample Lab Code	Brand Origin and Packaging Label	Sample's Color Number & Appearance
SH2X7	(US Origin) Makeup Kit	Pressed Powder, Matte Dark Brown
SH2X8	(US Origin) Makeup Kit	Pressed Powder, Matte Dark Olive
SH2X9	(US Origin) Makeup Kit	Pressed Powder, Matte Sliver
SH2X10	(US Origin) Makeup Kit	Pressed Powder, Shimmery Grey
SH2X11	(US Origin) Makeup Kit	Pressed Powder, Matte Plum
SH2X12	(US Origin) Makeup Kit	Pressed Powder, Matte Bluish Grey
SH2X13	(US Origin) Makeup Kit	Pressed Powder, Shimmery Sliver
SH2X14	(US Origin) Makeup Kit	Pressed Powder, Shimmery Black
SH2X15	(US Origin) Makeup Kit	Pressed Powder, Coral
SH2X16	(US Origin) Makeup Kit	Pressed Powder, Shimmery Peach
SH2X17	(US Origin) Makeup Kit	Pressed Powder, Shimmery Pearl
SH3X1	(US Origin) Cosmetics	SP031 Diverse, Pink
SH3X2	(US Origin) Cosmetics	SP030 Reluctance, Dark Green
SH4	(US Origin) Pigment	Shimmery White
SH5	(Us Origin) Eyeshadow	Shimmery Pearl, #Midnight Cowboy
E1	(Hong Kong Origin) Eyeliner Kajal	Black Semi-Soft
E2	(Germany Origin) - Eye Pencil	No. SM003, Black
E3	(China Origin) Lip/Eye Pencil	Green
E4	(Germany Origin) Line and Shadow Pencil	#17 color: Turquoise
E5	(China Origin) Eye Pencil- Medical Kohl	Black, solid
E6	(China Origin) - Original 1	Color #33, Black
E7	(France Origin), Waterproof Kohl Kajal	Black #001
E8	(Czech Republic Origin) Smoky-I Kohl Liner	Black 01
EB1X1	(China Origin) Coffee -Contour Externe	Pencil-color: brown
EB1X2	(China Origin) Wheat -Contour Interne	Pencil- color: beige
EB2	(China Origin) Eyebrow Kit	Brown pressed powder #medium
B2	(Us Origin) Makeup Kit	Pressed powder, orange red
B3	(US Origin) Blusher	shimmery peachy
B4	(Italy Origin) Stunning Matte Baked Blush	Peach Twist #06
B5	(China Origin) Cream Blush	creamy shimmery peachy #CB13 Tickled
F1X1	(Korea Origin) Bb Cream	Light Nude shade cream
F1X2	(Korea Origin) Bb Cream SPF50+ Pa+++	Nude shade cream
F1X3	(Korea Origin) Bb Cream SPF40+	Dark nude shade cream
F2	(Korea Origin) Snail Clearing Bb Cream, SPF 38/Pa+++	Dark nude shade cream
C1	(Jordan Origin) Whitening Cream	White cream

Sample Lab Code	Brand Origin and Packaging Label	Sample’s Color Number & Appearance
C2	(Thailand Origin) Facial Cream for Acne and Dark Spots	Yellowish cream
C3	(Indonesia Origin) Cream	Yellowish cream
C4	(Unknown Origin) Perfumed Cream for Hair and Body	Yellow jelly cream
C5	(US Origin) Concealer	Color #01 Light
C6	(Spain Origin) Crème	Yellowish cream
C7	(Lebanon Origin) Crème	Yellowish cream
C8	(India Origin) Advanced Multi Vitamin	Creamy
C9	(China Origin) HD Concealer	GC974 Nude
C10	(China Origin) HD Concealer	Medium Beige
C11X1	(China Origin) Color Correct Concealer Palette	Yellow (evens skin tone)
C11X2	(China Origin) Color Correct Concealer Palette	Green (redness corrector)
C11X3	(China Origin) Color Correct Concealer Palette	Purple (brightness skin tone)
C11X4	(China Origin) Color Correct Concealer Palette	Beige (light)
L2	(Unknown Origin) Crystal Shine Rouge	Shimmery light pink, color: #PK01
L3	(Taiwan Origin) Lipstick	# 33 Light green, semi-solid
L4	(Czech Republic Origin) Lip Color Crayon	Color #333, Chili
L5	(EC Origin) Lipstick	Color #212, Irish Coffee Sheer
L6	(China Origin) Lipstick	Color #911D, Stoplight Red
L7	(US Origin) Lipstick, Mini Size	Red
L8	(Italy Origin) Lipstick	Maroon
L9	(China Origin) Lip Gloss, Long Lasting	Red
L10	(Italy Origin) Charming Matte Lipstick	Color: Desert Rose #06
L11	(Unknown Origin) Lipstick	#Lc45
L12	(Saudi Arabia Origin) Lipstick	#21
L13	(Germany Origin) Waterproof Lipstick	#1303
L14	(Germany Origin) Lipliner	Cute Pink #07
L15	(China Origin) Liquid Lipstick	Red #10
L16	(Taiwan Origin) Long Lasting & Non-Transfer	# 77
L17	(China Origin) Long-Lasting Lip Gloss	#14
L18	(Unknown Origin) Matt Velvet Lipstick	24
L19	(Germany Origin) Long Lasting Lipstick	Fl #07
L20	(Turkey Origin) Watermelon Lip Balm	Watermelon
L21	(Unknown Origin) Lip Balm	Clear
L22	(US Origin) Long Lasting Liquid Color	Bella
L23	(Canada Origin) Shine Liquid Lipstick	Must Have Pink

Sample Lab Code	Brand Origin and Packaging Label	Sample's Color Number & Appearance
L24	(Unknown Origin) Velvet Matte Lipstick	75329 Orchid
L25	(Unknown Origin) Velvet Matte Lipstick	75330 Brick
L26	(US Origin) Pencil Lip Liner	Autumn
L27	(US Origin) Matte Liquid Lipstick	Autumn
NP1	(China Origin) Nail Polish	White
NP2	(Unknown Origin) Nail Polish	Shimmery Light Pink
NP3	(China Origin) Nail Polish	Glittery Golden, Color: 48
NP4	(China Origin) Nail Polish	Q1-18
NP5	(Turkey Origin) Nail Enamel	427 Sandstone
NP6	(US Origin) Nail Polish	104 Scarlett O'hara
NP7	(US Origin) Nail Polish Colors Professional	1520 Standing Bloom Only
NP8	(China Origin) Matte	Brown #26
NP11	(Turkey Origin) Matte Nail Enamel	Stylish Cyan #M05
NP12	(France Origin) Nail Paint Anti Shock System	Cold Pink #510
NP13	(China Origin) Nail Polish	Q2-5
NP14	(Unknown Origin) Professional Nail Polish	Brown
NP15	(Italy Origin) Gel Finish Nail Enamel	Purple
NP16	(Unknown Origin) Nail Polish	Nude #17
NP17	(China Origin) Nail Polish	White #49
NP18	(China Origin) Nail Polish	Purple #140
NP19	(Turkey Origin) Nail Color	Red #40
H1	(US Origin) Highlighter*	Pearly, Golden Color
H1-2	(US Origin) Highlighter*	Pearly, Golden Color
H1-3	(US Origin) Highlighter	Pearly, Golden Color
D1	(China Origin) Black Hair Dye	Black Powder, Color #1, Natural black
LO1	(US Origin) Dry Skin Moisturizer Lotion	White
MS1	(China Origin) Mascara Waterproof	Black
MS2	(US Origin) Mascara	Very Black
HR	(Saudi Arabia Origin) Henna Black Paste	Black paste
BC	(Thailand origin) DD cream	White

* Unknown Origin Counterfeit

VITA

Sahr Ayesh Alsherari

Candidate for the Degree of

Doctor of Philosophy

Dissertation: INDIRECT DETERMINATION OF MICA VIA RUBIDIUM CONTENT AND DIRECT DETERMINATION OF HEAVY METAL LEAD IN COSMETICS

Major Field: Chemistry

Biographical:

Education:

Completed the requirements for the Doctor of Philosophy in chemistry at Oklahoma State University, Stillwater, Oklahoma in December 2019.

Completed the requirements for the Master of Science and Technology in Chemical Analysis and Laboratory Management at University of New South Wales, Sydney, NSW, Australia in 2011.

Completed the requirements for the bachelor's degree in chemistry at Al Jouf University, Al Qurayyat, Saudi Arabia in 2008.

Experience:

Chemistry Lecturer - September 2012 to December 2014 - University of Tabuk

Freshmen Year Supervisor - May 2013 to May 2014 - University of Tabuk

Selected Abstracts:

August 2019-"Detection of Toxic Metal Contaminations in Cosmetics Using MP-AES and X-Ray Fluorescence", S. Alsherari, A.W. Apblett , ACS National Meeting, San Diego, CA, USA

October 2019-Indirect Determination of Mica Present in Cosmetics Via Rubidium Content" S. Alsherari, A.W. Apblett, Midwest Regional Meeting (MWRM) of the ACS. Wichita, Kansas, USA

Professional Memberships: American Chemical Society