Materials Composition and Toxicology of Cosmetic Products

A Senior Project

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By

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Project Title: Materials Composition and Toxicology of Cosmetic Products

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Abstract

In today's modern society, the U.S. Food and Drug Administration regulates many industries to protect consumers' health; the cosmetics industry is not one of them. Through self-regulation, companies continue to sell products for topical use on the body that have been known to contain toxic chemicals with little to no testing on the effects they have on the human body.

The purpose of this project was to determine the content of such known toxins in five different brands of face powders. X-Ray Diffraction (XRD) was used to verify the primary component and Inductively Coupled Plasma-Optical Emissions Spectroscopy (ICP-OES) was used to find trace metals. Analysis revealed that the predominant component was talc and mica, with trace concentrations of nickel (0.5-3 ppm), lead (0.5-3 ppm), and copper (0.75-2.8 ppm) in all the brands, chromium (4.25 ppm) in one brand, and relatively high amounts of iron (2690.25-11307.5 ppm) in all of the samples. While ICP-OES cannot discern the form of the element (ionic or elemental), these findings raise concerns about the long-term use of these products.

Key Words: Cosmetics, Face Powder, Heavy Metals, Toxicity, ICP-OES, XRD

Introduction

The use of cosmetics by humans predates written history. They have been used by many different cultures for various reasons such as traditional, artistic, or aesthetic purposes. Some compounds that have been used for cosmetic purposes vary from malachite, green copper ore, galena, khol, mercuric sulfide and white lead[1] in ancient times to phthalates, iron oxides, parabens, alkylphenols, synthetic musks, and many others in today's modern society[2].

In the modern United States, using compounds such as mercuric sulfide and white lead for cosmetic purposes would be frowned upon because of their widely known toxicological effects, but what about the effects of other compounds that are used in cosmetics today? Many people believe that all cosmetic products are safe since the cosmetics industry is regulated by the U.S. Food and Drug Administration (FDA) but in reality the cosmetics industry is self-regulated and has been since 1938[3]. Some research and testing has been done to study the effects of using cosmetic products but little effort is being made to make sure that the consumers know the risks of using such products.

Motivation

Many consumers feel safe using cosmetic products because they think that the FDA is in place to protect consumers from any harmful substances that may be present in the products. However, on FDA.gov, it states that the "FDA's legal authority over cosmetics is different from our authority over other products we regulate...Under the law, cosmetic products and ingredients do not need FDA premarket approval."[3] This means that cosmetic products can regularly be put on the market without any testing done by the FDA.

On the website, it also states that "neither the law nor FDA regulations require specific tests to demonstrate the safety of individual products or ingredients. The law also does not require cosmetic companies to share their safety information with FDA."[3] So not only do

companies have the liberty to put products on the market without FDA approval, but they are not even required to do testing to ensure the safety of the product and ingredients nor do they have to report any of this information to the FDA. It is estimated that only about 13 percent of the more than 10,500 chemicals found in cosmetics and other beauty products have been fully tested for their impact on health.[2]

The cosmetics industry regulations were determined in the late 1930s when it was assumed that the skin is an impermeable barrier that prevents chemicals from penetrating into the body. It is now know that this is not true, yet most consumers and cosmetic companies are concerned only with allergic reactions and skin irritations.[4] But one must also consider systemic absorption, toxicity, and chronic effects. What degree of absorption is there when a cosmetic product is left on the face for twelve hours or spread over the entire body like suntan lotions? What are the long term effects of using such products? No one really knows because not enough testing has been done to ensure cosmetic products are thoroughly safe. It is imperative that this information is available to consumers so that they can make informed decisions about what products to purchase.

Experimental Design

This project aims to to raise consumer awareness about the potential risk that comes with the use of cosmetic products. The risk can be defined using the following simple equation:

$$\text{RISK} = \text{HAZARD} \times \text{EXPOSURE} \tag{EQ. 1}$$

where hazard is the inherent property or ability of a substance to cause an adverse or detrimental effect while exposure describes the route, frequency, duration, and magnitude of the contact an individual has with the hazardous substance.[5] This project focused on determining the exposure that a consumer will have to cosmetic products in a lifetime.

There are a wide variety of cosmetic products so the scope of this project was narrowed down to specifically face powders because it is considered a basic essential product in a

consumer's makeup routine and because it is applied to a large area. Since there are also many different brands that a consumer can choose from, the brands were narrowed down to Covergirl, e.l.f., Maybelline, NYC, and Rimmel London because they are all popular brands amongst the young and low income population which was the target population of this project. There are a lot of potential toxins within the face powder, but this project focused on heavy metals, specifically cadmium, chromium, copper, lead, iron, and nickel, because heavy metals can bioaccumulate in the body and cause harm to vital organs.

Two analytical methods were used to complete this experiment: x-ray diffraction (XRD) and inductively coupled plasma-optical emissions spectroscopy (ICP-OES). XRD was chosen as one of the methods because it would be ideal to verify the primary components in the face powders. Since it was suspected that the heavy metals in the face powder would be present in trace amounts, an analytical method that can detect trace levels had to be used which is why ICP-OES was chosen as the best analytical method.

Experimental Procedure

First, XRD was used to verify the primary components. X-ray diffraction uses a collimated x-ray beam as a probe and a detector to detect constructive interference of scattered x-rays to identify crystalline components in the sample. The software plots the intensity at a wide range of d values and a material can be identified by the pattern formed.

The face powder that was obtained was in the form of pressed powder, so the powder had to be loosened by scraping it using a small metal spatula. Then one gram of face powder was placed onto the powder sample holder as shown in Figure 1a. When using XRD, it is necessary to have a horizontally flat surface to optimize the x-ray interaction with the atoms in the sample and to obtain better, more accurate results so a glass slide, shown in Figure 1b, was used to achieve these results. The final prepared sample with a flat surface can be seen in Figure 1c. It was mounted into the x-ray diffractometer, shown in Figure 1d.

The diffractometer was equipped with a copper filter, a 0.2mm detector slit, and a 1mm divergence slit. The detector and divergence slit width was determined through a series of trials which were designed to find the best combination of divergence and detector slit widths that would give the best resolution. The sample was scanned from 4° to 75° at a scan speed of 5° per minute. The main components were then identified by using the EVA software to match the sample spectrum to the pattern that matched best.
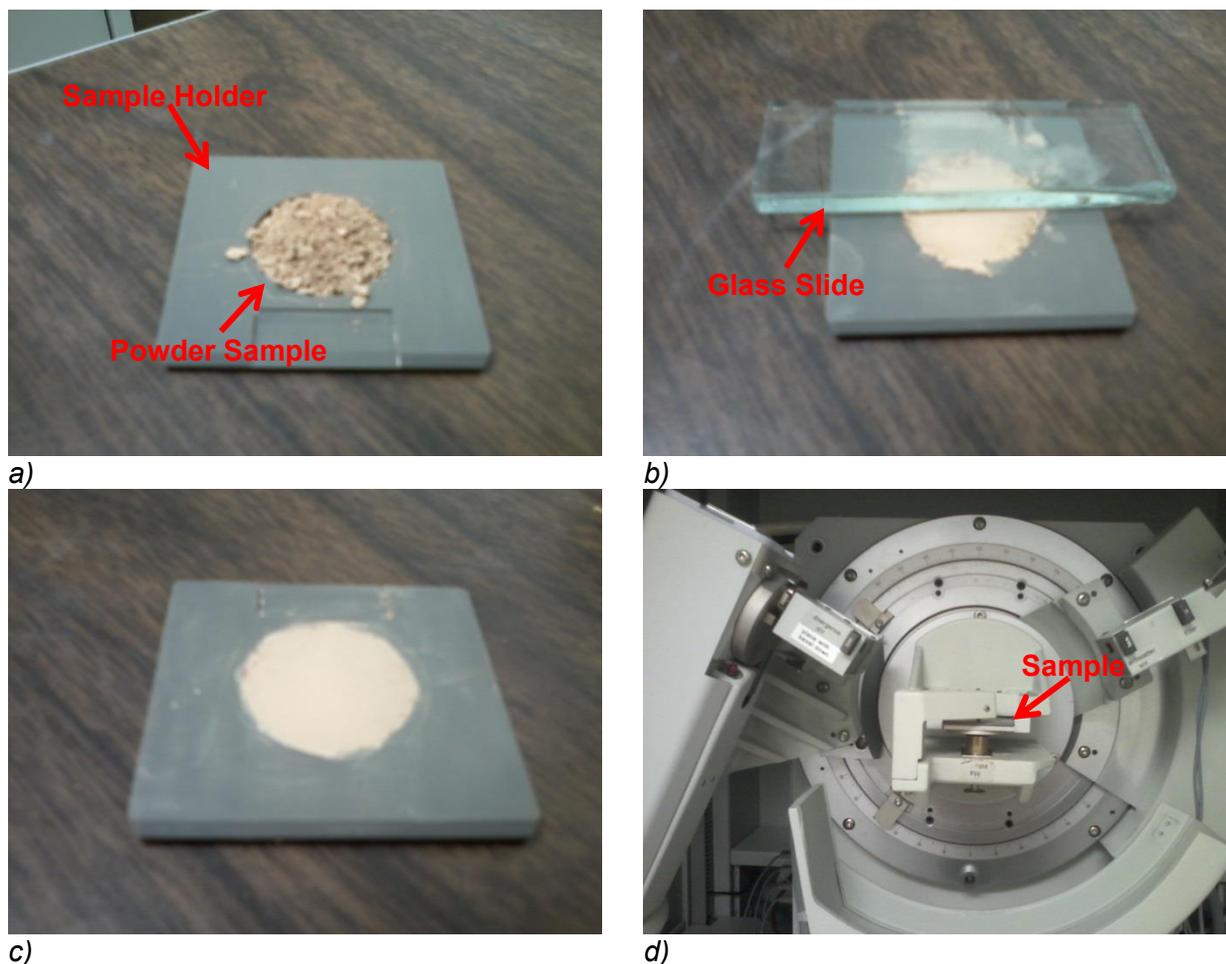
Figure 1: Example of the steps taken to prepare a sample for x-ray diffraction. a) One gram of loose powder on a sample holder. b) A glass slide being used to flatten the sample. c)The sample ready to be analyzed. d)The sample inside of the x-ray diffractometer.

To detect trace amounts of heavy metals, ICP-OES was used. ICP-OES is an analytical method that takes an acid digested solution sample, atomizes it using argon gas, and then uses inductively coupled plasma to excite atoms and ions which emit electromagnetic radiation. The

wavelengths from the electromagnetic radiation are characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

The samples had to be prepared by using a procedure called acid digestion which is a process that dissolves all organic matter in the sample. To begin, two grams of each sample were measured out using a scale with 0.01 gram precision and placed in a large test tube. Then 10mL of nitric acid were added into the test tube and thoroughly mixed using a sonicator. The samples were then cooked for 15 hours at 45°C and then digested for two hours at 105°C. Then 500 μL of 30% hydrogen peroxide were added, which caused the sample to effervesce. Once the effervescence subsided, an additional 500 μL of 30% hydrogen peroxide were added and then 50 mL of distilled water.

After the acid digest, the samples were a mixture of powder and solution, shown in Figure 2a. The solution had to be separated from the solid particles, so a large 20mL syringe equipped with a 0.45μm polyvinylidene chloride (PVDC) syringe filter, shown in Figure 2b, was used to aspirate the solution. The filters were designed to fit into the tubes to create a seal so that the tube can be turned upside down and the solution would not spill out, which can be seen in Figure 2c. The solution was aspirated out by fitting the filter into the tube, turning it upside down, and pulling on the syringe plunger. The 20mL sample that was aspirated was transferred to the small capped containers shown in Figure 2d. The remaining sample was a solution that had almost no organic matter in it. The samples were then ready to be analyzed using the ICP-OES shown in Figure 2e.

The machine was then calibrated using a standard solution that had chromium, copper, cadmium, iron, lead, and nickel amongst other metals at a concentration of 50 PPB, which is shown in Figure 2f. To calibrate the machine, the standard was introduced into the system in calibration mode and the electromagnetic radiation was measured. Once the machine was calibrated, the samples were introduced into the machine and analyzed one by one and compared to the electromagnetic radiation of the standard.
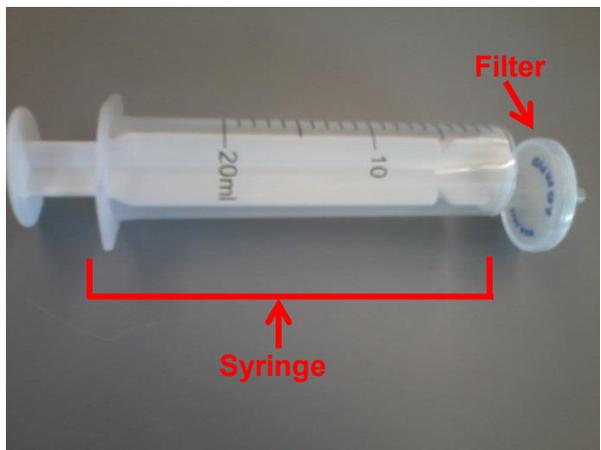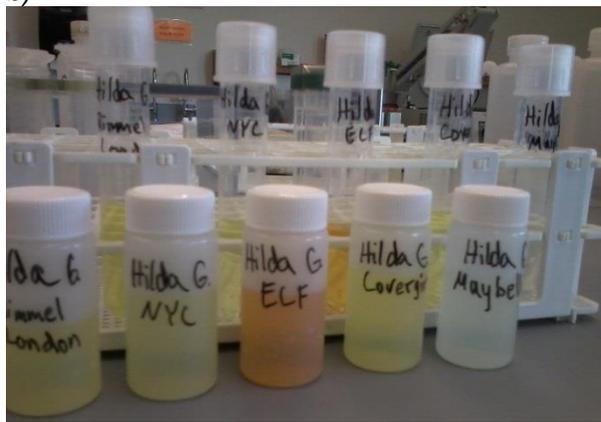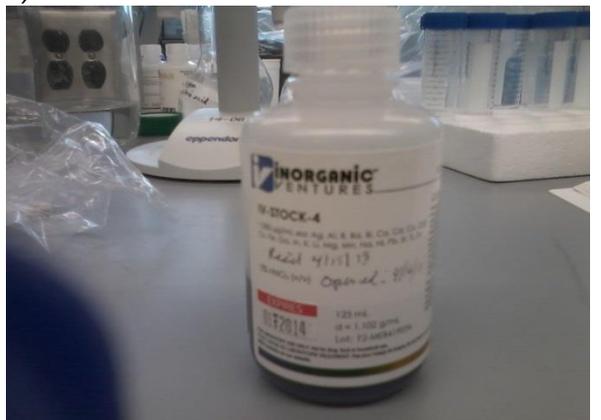
Figure 2: The sample preparation for inductively coupled plasma-optical emission spectroscopy (ICP-OES). a) The samples as they looked after the acid digest. b) The 20mL syringe with the 0.45µm polyvinylidene chloride (PVDC) syringe filter used to aspirate the solution. c) A sample image of how the solution was aspirated d) The samples ready to be analyzed. e) The standard that was used to calibrate the ICP-OES. f) The ICP-OES machine used to analyze the samples.

Results

A sample graph of the XRD scan results is shown in Figure 3. The rest of the graphs can be seen in Appendix A. To verify the main components, the pattern database on the EVA software was used. The database assigns every pattern a quality mark that ranges from "High Quality" for high quality measured patterns, "Calculated" for patterns obtained by computation from the structure, and "Indexed" for good quality measured patterns, to "Questionable" for patterns not meeting the minimum requirements for "Indexed" quality mark, "Not Specified" for patterns not matching the requirements for a "Questionable" quality mark, and "Deleted" for patterns that have been replaced by other patterns. It is best to use patterns that have a High Quality quality mark, but Calculated or Indexed quality marks are acceptable.

NYC - File: NYC.raw - Type: 2Th/Th locked - Start: 4.000 ° - End: 75.000 ° - Step: 0.100 ° - Step time: 1.2 s - Temp.: 25 °C (Room) - Time Started: 1400382336 s - 2-Theta: 4.000 ° - Theta: 2.000 ° -
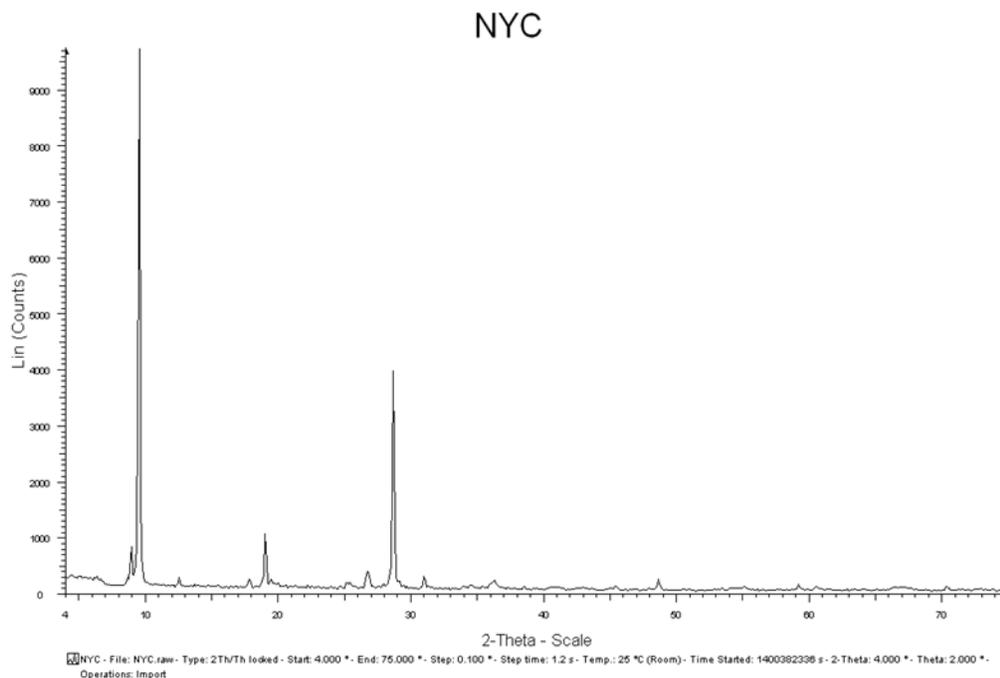Operations: Import

Figure 3: A sample graph of an XRD scan. The intensity is on the y-axis while the 2Θ *angle is* on the x-axis.

The XRD scans were compared to the patterns from the database. Since some of the patterns were determined through computations and others were determined experimentally, if the 2Θ angle matched an intensity peak and was within 5% of the angle, then it was considered

a match. All of the intensities were carefully examined and the matched peaks were identified and marked on the graph. A sample graph is shown in Figure 4. The remainder of the graphs can be seen in Appendix B. Using this method, talc and mica, which both had Calculated quality marks, were identified as the main components in the e.l.f., Maybelline, NYC, and Rimmel London brands, but for Covergirl, only talc was verified as a main component. Although many of the large peaks were identifiable, some peaks were not able to be matched with the patterns in the database. This may suggest that there are some components that are unknown.
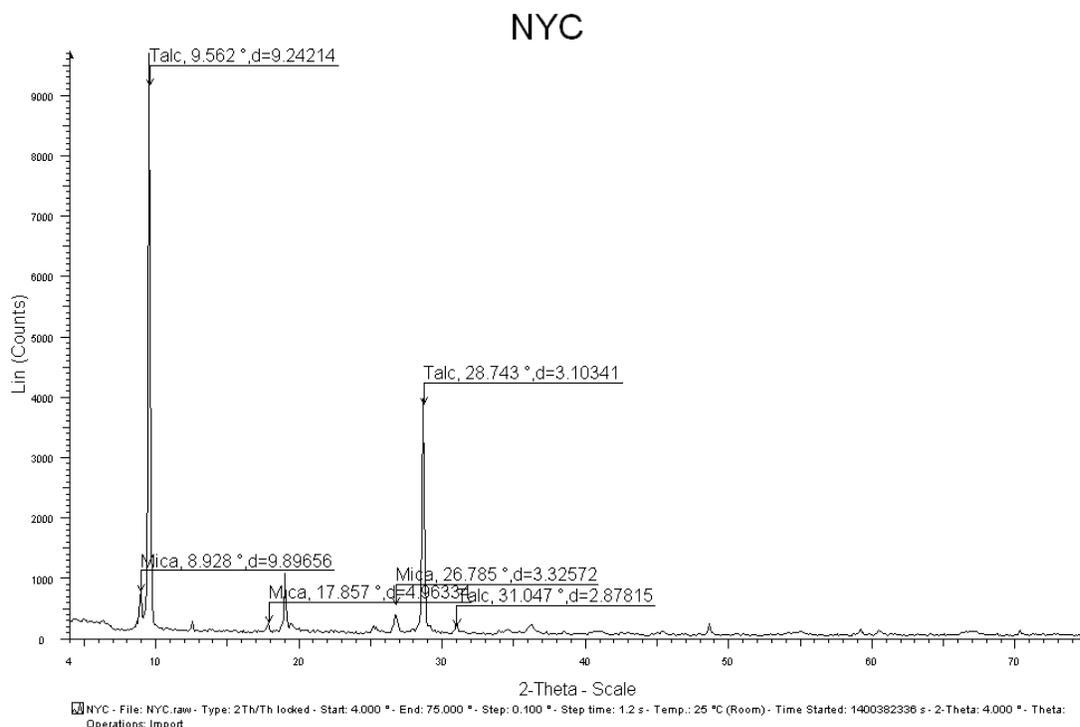
Figure 4: A graph of the intensity peaks that matched the database patterns.

XRD was also essential in determining the analysis method used to identify the heavy metals in the samples. Since it was apparent that the talc and mica were the predominant component, it was assumed that any metal in the powder would be present in trace amounts. Initially, energy dispersive spectroscopy (EDS) was the analysis method of choice, but since the detection limit for EDS is about 1000 parts per million (PPM), a different method that could

measure trace amounts would have to be employed. Further research led to the decision that ICP-OES would be a better method for this application. ICP-OES has an instrument detection limit (IDL) that is determined experimentally by the machine. Table I shows the IDL for the metals in parts per billion (PPB) which ranges from 10 PPB to 112 PPB. ICP-OES has the sensitivity needed to identify the heavy metals at the desired level.

Table I: Instrument Detection Limit of ICP-OES

Cadmium (PPB)	Chromium (PPB)	Copper (PPB)	Iron (PPB)	Nickel (PPB)	Lead (PPB)
10.4	74.6	16.7	112.0	17.7	10.0

Through ICP-OES, trace amounts of copper, nickel, and lead were found in all the samples, chromium was found in one of the samples, and relatively high amounts of iron were found in all samples, but no trace amount of cadmium was detected in any of the samples. The raw data collected can be seen in Table II. The data shown in the table is the PPB detected in the solution.

Table II: Raw Data from ICP-OES (PPB in Solution)

Sample Name	Cadmium (PPB)	Chromium (PPB)	Copper (PPB)	Iron (PPB)	Nickel (PPB)	Lead (PPB)
Covergirl	0	0.060	0.040	107.61	0.020	0.060
Maybelline	0	0.070	0.110	452.30	0.050	0.120
e.l.f.	0	.170	0.030	1,148.00	0.0120	0.070
NYC	0	0.040	0.040	112.08	0.020	0.020
Rimmel	0	0.070	0.030	334.96	0.040	0.060

The results from the ICP-OES were converted into parts per million (PPM) in the dry sample by multiplying the amount by 50mL since the solution used was diluted to 50mL and then it was divided by 2 grams because that was the original sample size. The values are reported in Table III in PPM.

Table III: PPM in Dry Sample

Sample Name	Cadmium (PPM)	Chromium (PPM)	Copper (PPM)	Iron (PPM)	Nickel (PPM)	Lead (PPM)
Covergirl	0	<IDL	1	2690.25	0.5	1.5
Maybelline	0	<IDL	2.8	11307.5	1.25	3
e.l.f.	0	4.25	0.75	28700	3	1.75
NYC	0	<IDL	1	2802	0.5	0.5
Rimmel	0	<IDL	0.75	8374	1	1.5

Since the purpose of the project was to find the exposure to heavy metals in a lifetime, the data collected was converted to exposure in a lifetime by making some assumptions. It was assumed that the average consumer uses face powder for fifty years of their life, that a consumer uses four cases of face powder a year, and that a case of face powder contains eight grams of product. Using these assumptions, it was calculated that the average consumer is exposed to 1,600 grams of product. This number along with the data from Table III was used to determine the exposure in a lifetime, shown in Table IV.

Table IV: Consumer Exposure Time in Lifetime

Sample Name	Chromium (mg)	Copper (mg)	Iron (mg)	Nickel (mg)	Lead (mg)
Covergirl	NA	1.6	4304.4	0.8	2.2
Maybelline	NA	4.5	18092	1.9	5.4
e.l.f.	6.8	1.2	45920	5.1	3.2
NYC	NA	1.6	4483.2	0.8	0.8
Rimmel	NA	1.2	13398.4	2.0	2.5

Discussion

The analytical methods used in this project confirmed that the main components of the face powder of these five brands were talc and mica. Trace amounts of copper, nickel, lead, and iron were detected in all samples while chromium was detected in one of the samples. The exposure to heavy metals was determined experimentally. Since the risk model in Equation 1 has two parts to it, the hazard and the exposure, the hazard should also be considered when analyzing the risk of cosmetic products. The Material Safety Data Sheets (MSDS) for each of these metals were consulted[6]. Certain data was pulled from the MSDS and charted on Table V. The categories looked at were carcinogenic effects (causes mutations that cause cancer), mutagenic effects (causes mutations that don't cause cancer), teratogenic effects (can cause congenital abnormalities), developmental effects (abnormalities that manifest during human development,), skin irritants, permeators (a material that can permeate the skin), and the health hazard rating assigned to each metal.

Table V: Hazardous Effects of Metals

	Copper	Chromium	Nickel	Lead	Iron
Carcinogenic			✓	✓	
Mutagenic	NA	NA	NA	NA	NA
Teratogenic	NA	NA	NA	NA	NA
Developmental	NA	NA	NA	NA	NA
Skin Irritant	✓	✓	✓	✓	✓
Permeator	✓	✓	✓	✓	✓
Health Hazard	2	2	2	1	1

It was found that nickel and lead are both listed as carcinogenic, all metals were listed as skin irritants, and all metals were listed as permeators. The mutagenic, teratogenic, and developmental effects were not available on the MSDS, but just because the data is not available it does not mean that the effects are not existent; it may mean that not enough studies

have been done to determine the effects of these metals. It is true that some heavy metals such as iron and copper are necessary for natural bodily functions, but too much of a good thing can be bad. These heavy metals can be absorbed through the skin, get into the bloodstream, and have access to all the organs where they can bioaccumulate and cause damage to the body.

Metals enter the body in different ways. For example, lead can be either inhaled or ingested. Once in the body, it can travel to the bloodstream, build up in the organs, and eventually enter the bones and teeth where it can stay for decades.[7] Cadmium enters the body through inhalation or ingestion and accumulates in the kidneys and liver where it can remain for many years. A small portion of the cadmium that enters your body leaves slowly in urine and feces. The body can change most cadmium to a form that is not harmful, but too much cadmium can overload the ability of the liver and kidney to change the cadmium to a harmless form.[8] Nickel can be inhaled, ingested, and absorbed through the skin. It builds up in the blood and bones and leaves the body in the urine.[9] Chromium can enter the body by inhalation, ingestion, and skin absorption. It can accumulate in soft tissues and organs and leave the body through urine.[10] Although some of the metals that are introduced into the body can be excreted, the excretion rate is not equivalent to the absorption rate.

Metals in the body are harmful for different reasons. Lead is a proven neurotoxin that is linked to learning, language and behavioral problems. It has also been linked to miscarriages, reduced fertility in men and women, hormonal changes, menstrual irregularities, and delays in puberty onset in girls.[7] Cadmium, although it was not found in any of the samples, is known to cause cancer and targets the body's cardiovascular, renal, gastrointestinal, neurological, reproductive, and respiratory systems.[8] Nickel exposure has been known to cause chronic bronchitis, reduced lung function, and cancer.[9] Chromium is also strongly linked to immune and respiratory toxicity as well as systemic toxicity.[10] Additionally, iron, nickel, chromium, cadmium, and lead have been found in cancerous breast biopsies as opposed to biopsies taken from women without breast cancer.[5]

Conclusion

Through this project, no direct connection can be made between these specific brands of face powder and any kind of organ or bodily damage, but finding trace levels of these metals should raise concern amongst consumers, especially the lead detected. ICP-OES cannot distinguish between elemental or ionic form, so it would be interesting to be able to discern this in future work. Additionally, analysis of the effects of particle size on the absorption rate would be interesting to know. It would also be interesting to access the risk of higher end brands as opposed to the lower end brands that were analyzed in this experiment to see if paying more money for cosmetics decreases the risk of using the products. Although this project focused on finding trace metals in face powder, additional testing for other toxins should be done and also testing other cosmetic products such as eye shadow, mascara, eyeliner, or lipstick for toxins would be essential to decrease consumer risk and increase consumer safety.

Acknowledgement

  I would like to thank the Cal Poly Materials Engineering Department for providing the equipment and lab space to do my senior project, my senior project advisor Dr. Trevor Harding for his guidance and support throughout this entire process, Dr. Linda Vanasupa for helping me define my project and for giving me wonderful advice and insight, and Dr. Chip Appel and Craig Stubler of the NRES Department for letting me use the ICP-OES and helping me analyze my samples.
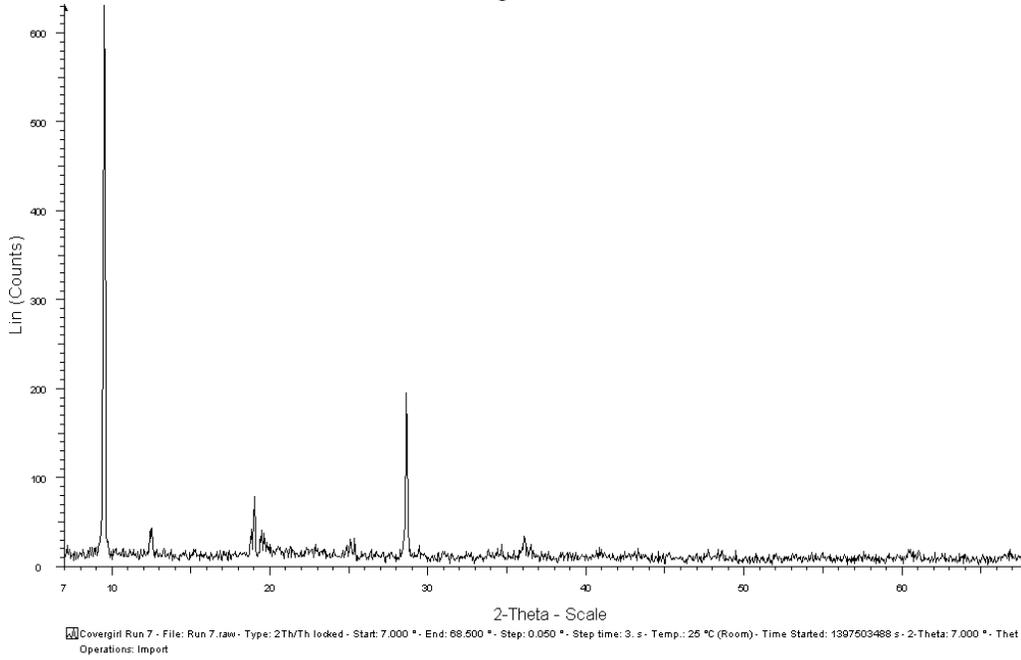
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10. Environmental Health Perspect 121:A196 (2013). http://dx.doi.org/10.1289/ehp.121-a196 [online 01 June 2013].

Appendix A

Original XRD Graphs

Covergirl

e.l.f.
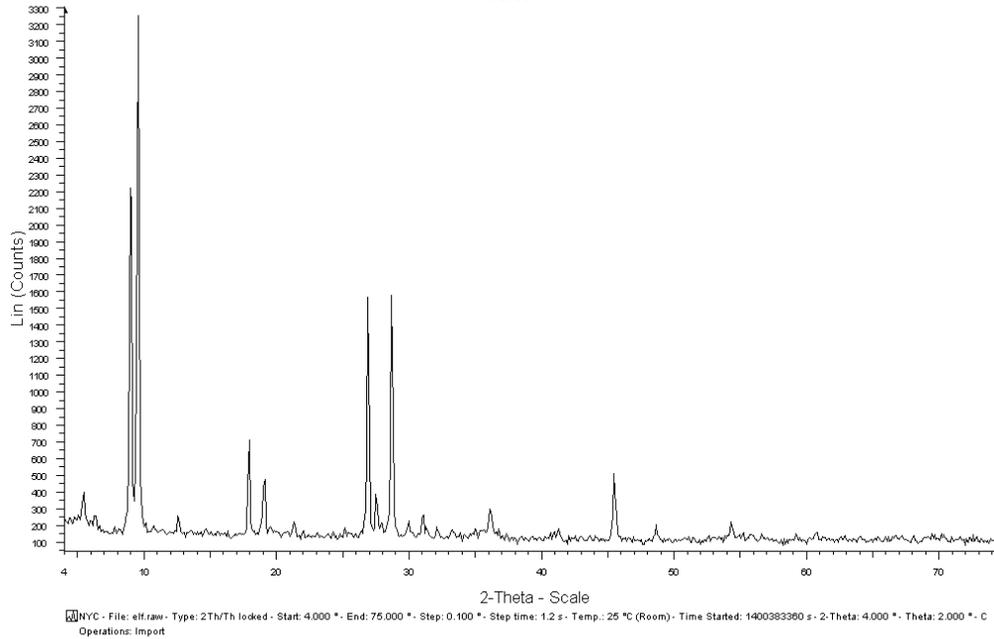
Maybelline

Maybelline - File: Maybelline.raw - Type: 2Th/Th locked - Start: 4.000 ° - End: 75.000 ° - Step: 0.100 ° - Step time: 1.2 s - Temp.: 25 °C (Room) - Time Started: 1400381056 s - 2-Theta: 4.000 ° - Th
Operations: Import
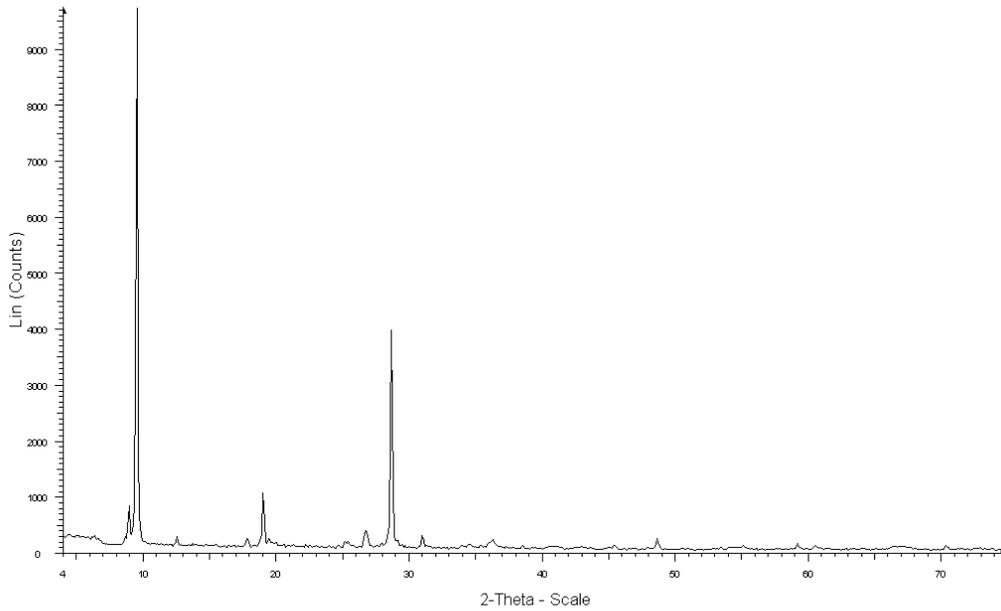
NYC

NYC - File: NYC.raw - Type: 2Th/Th locked - Start: 4.000 ° - End: 75.000 ° - Step: 0.100 ° - Step time: 1.2 s - Temp.: 25 °C (Room) - Time Started: 1400382336 s - 2-Theta: 4.000 ° - Theta: 2.000 ° -
Operations: Import

Rimmel London

Rimmel London - File: Run 1.raw - Type: 2Th/Th locked - Start: 4.000 ° - End: 75.000 ° - Step: 0.100 ° - Step time: 1.2 s - Temp.: 25 °C (Room) - Time Started: 1400379648 s - 2-Theta: 4.000 ° - Th
Operations: Import

Appendix B

XRD Graphs with Matched Peaks

Covergirl

Talc, 9.479 °,d=9.32263
Talc, 28.687 °,d=3.10938
Talc, 19.008 °,d=4.66514

Covergirl Run 7 - File: Run 7.raw - Type: 2Th/Th locked - Start: 7.000 ° - End: 68.500 ° - Step: 0.050 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 1397503488 s - 2-Theta: 7.000
Operations: Import

e.l.f.

Talc, 9.503 °,d=9.29934
Mica, 8.985 °,d=9.83464
Talc28.682 °,d=3.10995
Mica, 26.896 °,d=3.31220
Mica, 17.969 °,d=4.93247
Mica, 19.063 °,d=4.65174
Talc, 27.530 °,d=3.23740
Mica, 45.557 °,d=1.98959

NYC - File: elf.raw - Type: 2Th/Th locked - Start: 4.000 ° - End: 75.000 ° - Step: 0.100 ° - Step time: 1.2 s - Temp.: 25 °C (Room) - Time Started: 1400383360 s - 2-Theta: 4.000 ° - Theta: 2.000 ° - C
Operations: Import

Maybelline

Mica, 8.868 °,d=9.96392
Mica, 26.834 °,d=3.31977
Mica, 17.736 °,d=4.99691
Talc, 9.616 °,d=9.18990
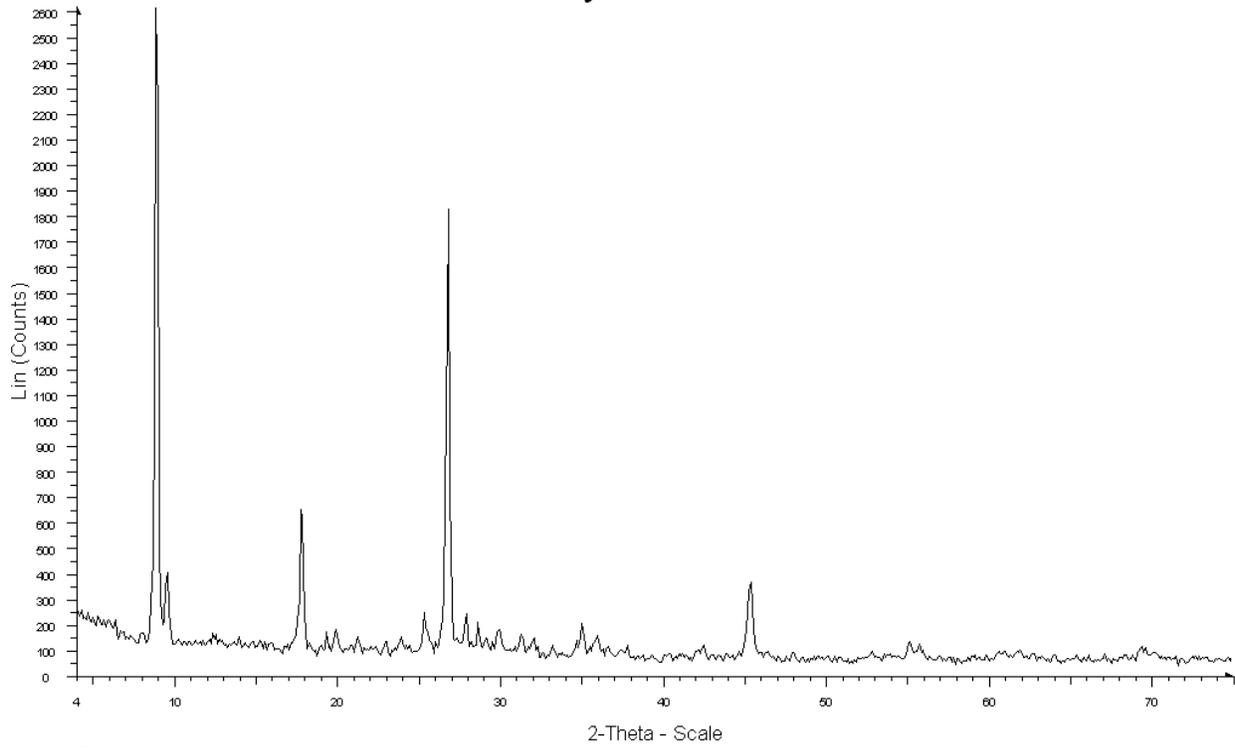Mica, 45.376 °,d=1.99710
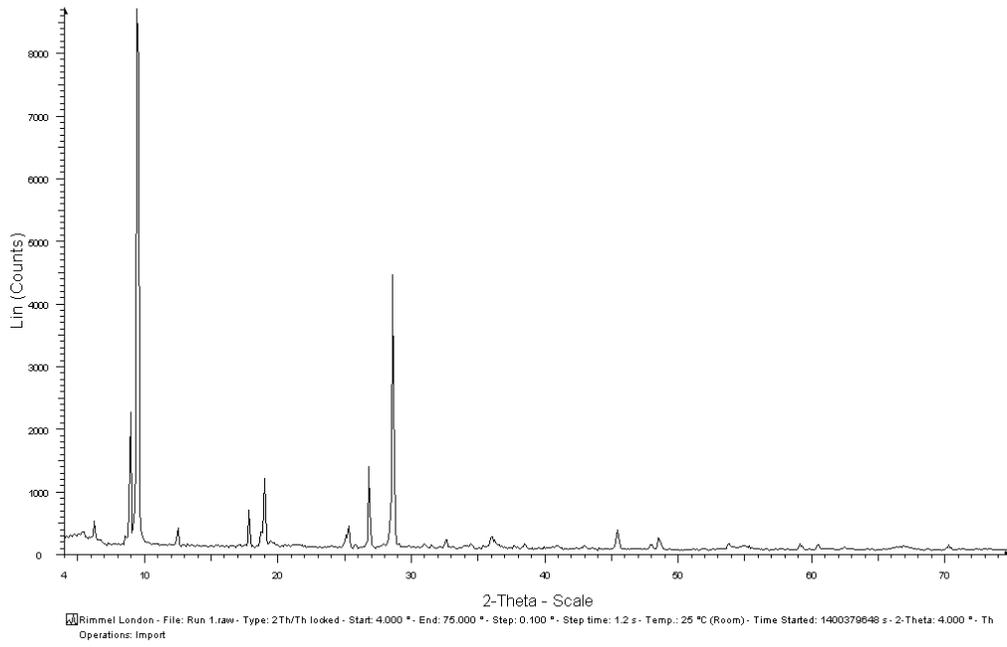Talc, 35.068 °,d=2.55682

Lin (Counts)

2-Theta - Scale

Maybelline - File: Maybelline.raw - Type: 2Th/Th locked - Start: 4.000 ° - End: 75.000 ° - Step: 0.100 ° - Step time: 1.2 s - Temp.: 25 °C (Room) - Time Started: 1400381056 s - 2-Theta: 4.0
Operations: Import

NYC

Talc, 9.562 °,d=9.24214
Talc, 28.743 °,d=3.10341
Mica, 8.928 °,d=9.89656
Mica, 26.785 °,d=3.32572
Mica, 17.857 °,d=4.9633Talc, 31.047 °,d=2.87815

Lin (Counts)

2-Theta - Scale

NYC - File: NYC.raw - Type: 2Th/Th locked - Start: 4.000 ° - End: 75.000 ° - Step: 0.100 ° - Step time: 1.2 s - Temp.: 25 °C (Room) - Time Started: 1400382336 s - 2-Theta: 4.000 ° - Theta:
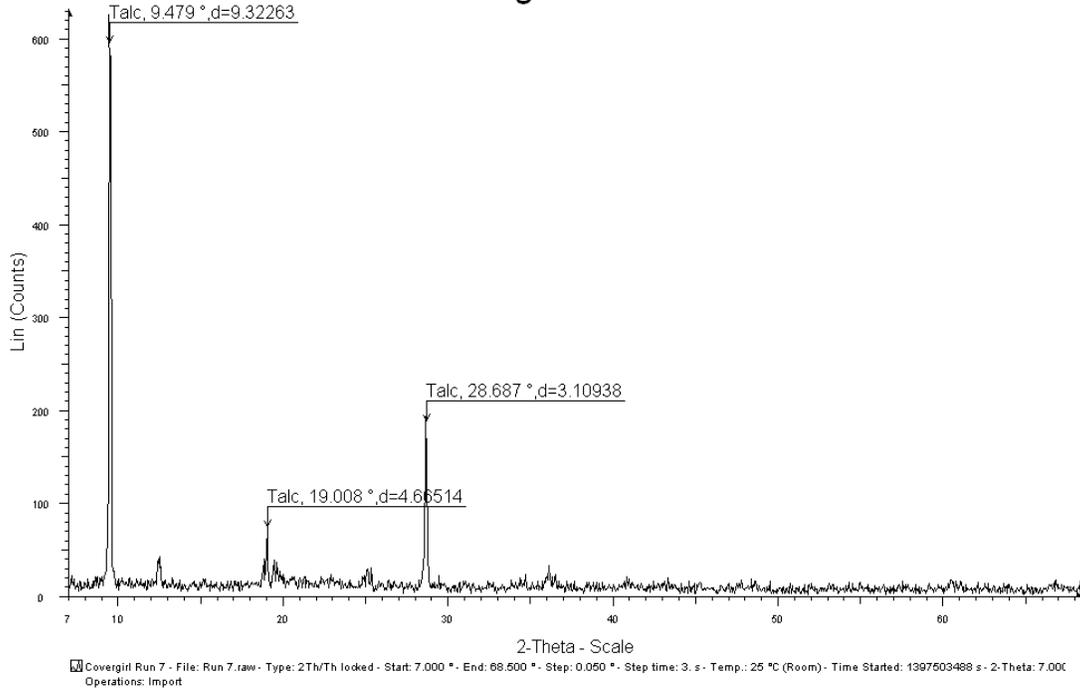Operations: Import

Rimmel London

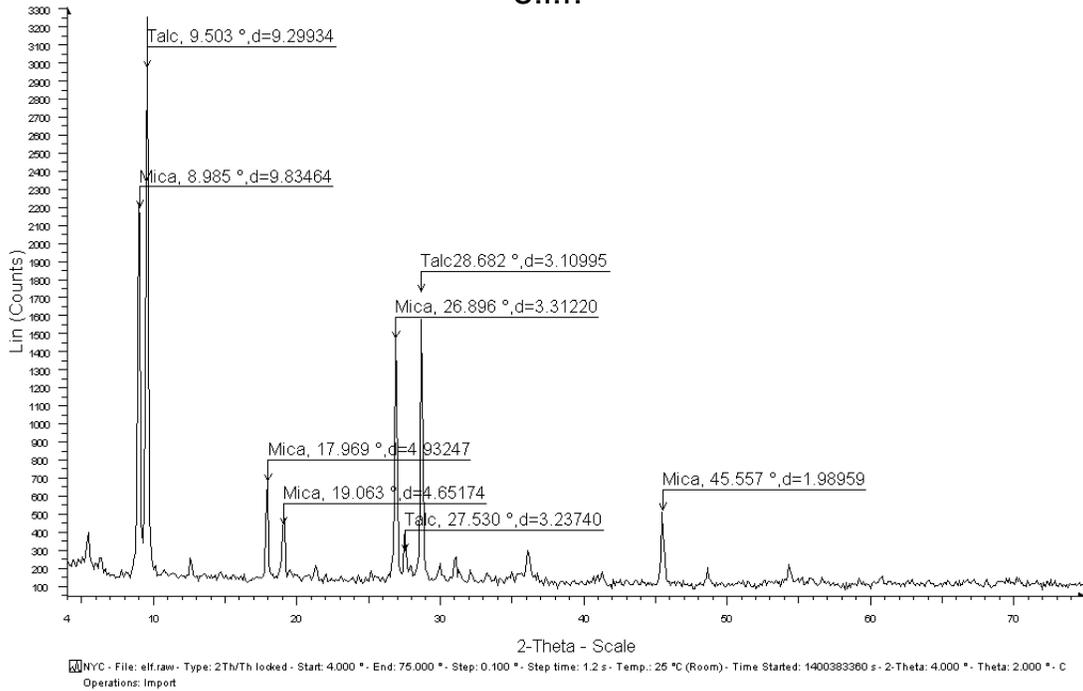XRD spectrum with axes "Lin (Counts)" (y-axis) and "2-Theta - Scale" (x-axis). Labeled peaks:
- Talc, 9.445 °,d=9.35591
- Mica, 8.927 °,d=9.89796
- Talc, 28.624 °,d=3.11607
- Talc, 19.063 °
- Mica, 26.781 °,d=3.32618
- d=4.65174
- Mica, 17.796 °,d=4.97997
- Mica, 45.557 °,d=1.98959

Rimmel London - File: Run 1.raw - Type: 2Th/Th locked - Start: 4.000 ° - End: 75.000 ° - Step: 0.100 ° - Step time: 1.2 s - Temp.: 25 °C (Room) - Time Started: 1400379648 s - 2-Theta: 4.0
Operations: Import