CHEMISTRY EXTENDED ESSAY

"An investigation on lead concentrations in different brands of lipsticks by using atomic absorption spectrometer assisted by microwave digestion"

Mertkan Koca

D1129-0045

Session: May 2014

Supervisor: Serenay Tarhan Güler

Word Count: 3705

TED Ankara College Foundation High School

Table of Contents

List of Figures

List of Tables

Mertkan Koca
D1129-0045

Abstract

Lipsticks are one of the most popular cosmetic products among women. Recently it is stated that some of the lipsticks involve heavy metals, such as Lead, which have cancerous effects, and since I have lady friends, family members and teachers around me using lipsticks, I decided to investigate this issue. Even though it is in small amounts, it can accumulate in body and increase its negative effects rapidly if the lipstick usage is ongoing. So, I decided to investigate the amount of lead in randomly selected lipsticks, since I couldn't access any literature value to compare because no company states the lead concentration in their products. My samples were Maybeline #475 Coral Diamonds, L'oreal #340 Sorbet Fraise Raspberry, Alix Avien #327, Golden Rose #216, and Pastel Lipstick #400.

An atomic absorption spectrometer was used to determine amount of Lead in lipsticks. Lipstick sample consists of other compounds rather than lead, the solid sample needed to be digested, so an acid mixture of HNO_3 and HF was used to prepare an aqueous solution. Though, the acid mixture itself is not sufficient enough to solve the lipstick sample. Microwave is used to assist the digestion process, which is the atomization stage, to obtain a homogenous solution. The research question is **"How do the lead concentrations of different brands of lipstick samples solved in acid mixture and determined by using atomic absorption spectrometer vary under standard atmospheric conditions and room temperature and to what extent do they have hazardous effects?"**

Unsurprisingly, Lead was present in all of the samples and the values were approximately close to each other, meaning all of the samples mount the risk of cancer when used perpetually. Still, the most risky one is Pastel Lipstick with a Lead amount of 0.6698 ng in 1 g of lipstick.

Word Count: 298

Acknowledgement

I would like to present my most sincere thanks to my supervisor, Serenay Tarhan Güler, for her perpetual concern and struggle during this assignment.

Also, I would like to present my thanks to our IB coordinator, Mustafa Üstünışık, for his courtesy and effort to supply needed equipment by contacting various universities and professors.

Furthermore, I would like to thank Emrah Özensoy, Assistant Professor in Physical Chemistry Department in Bilkent University, Prof. Dr. Yavuz Ataman, Professor in Middle East Technical University (METU), Erhan Özdemir, Research Assistant in METU in Analytical Chemistry Department, Sema Gündüz, Research Assistant in İstanbul Technical University (ITU) in Analytical Chemistry Department, and Prof. Dr. Süleyman Akman, Professor in ITU, for their unceasing interest and intention to help.

Finally, I would like to thank METU Analytical Chemistry Department for supplying microwave and atomic absorption spectrometer (AAS).

1.INTRODUCTION

Most of the cosmetic products contain toxic substances including heavy metals, especially lipsticks due to their ingredients. I decided to investigate Lead since it is one of the most dangerous heavy metals and have cancerous effects and can easily accumulate in human body.

1.1 Lead

Lead (Pb) is a highly toxic metal, which have cancerous effects on almost all of the organs of human body. It can be seriously hazardous even deadly when it passes a tolerable level in human body, which can lead to long-term health issues such as permanent brain damage. The symptoms of lead poisoning include weakness, vomiting, loss of appetite, convulsions and anemia in short-term. Lead exposure in body, by inhalation, swallowing or absorption through the skin, acts as poison. When the exposure reaches high levels in a short interval it is called acute toxicity. When it reaches high levels in a long time interval it is called chronic toxicity, which is what we are dealing in lipstick issue.

As soon as lead gets into a person's system, just like helpful minerals such as iron, zinc and calcium, it is distributed throughout the body. It causes harm anywhere it lands. For instance, it damages red blood cells in the bloodstream and lowers their oxygen carrying capacity to required tissues, which results in anemia.

Most of the Lead accumulates in the bone, where it has greater effects. It directly interferes with marrow and therefore with production of blood cells. Lead takes the Calcium ions, which bones need to grow strong and healthy, resulting unhealthy and weak bones.

Lead is much more harmful to children than adults because it can affect children's developing nerves and brains. The younger the child, the more harmful lead can be. Unborn children are the most vulnerable.

Possible complications include:

- Behavior or attention problems
- Failure at school
- Hearing problems
- Kidney damage
- Reduced IQ
- Slowed body growth

The symptoms of lead poisoning may include:

- Abdominal pain and cramping
- Aggressive behavior
- Anemia
- Constipation
- Difficulty sleeping
- Headaches
- Irritability
- Loss of previous developmental skills (in young children)

- Low appetite and energy
- Reduced sensations

The most significant step is to stop the access of the source of lead to the body. When this is done, treatment is not usually necessary if the blood lead level is less than 10 μg/dL. However, blood tests should be repeated regularly to check about the amount of lead in the bloodstream.

Treatment is required in higher levels of lead in the bloodstream. It consists of taking a special drug that binds to the lead and helps the body to remove it, which is called chelation therapy.

Though, very high levels of lead, which is 70 μg/dL or greater, require hospitalization to begin therapy.

Besides recommending a nutritious diet, the doctor also may recommend iron or calcium supplements. If a child with lead poisoning has iron-deficiency anemia, it is very important that the anemia be treated. Anemia puts the child at higher risk.

Even though most of the lead contamination is from leaded gasoline, lead-based paints, lead in water systems and lead solder for sealing cans in which food is stored are reduced, people are still concerned about the existence of possible lead sources. Lead in gasoline and paint can pass to soil and dust in there for many years and used especially in food and cosmetic products.

1.2 Lipsticks and Lead

Different brands of lipsticks include different amounts and types of waxes, polishes, emollients, oils, antioxidants, dye pigments and filling materials like silica, mica, titanium dioxide and fish scales which give lipsticks different colors, smells, appearances, brightness and texture. Lead is not one of basic ingredients of lipsticks, though most of them contain it because they can originate from ingredients listed above. The ingredients may include lead naturally or a result of contamination, for instance lead accumulated in fish as a result of pollution, also lead can simply pass into ingredients from the containers they are kept in or during production. US FDA (United States Food & Drug Administration) detected lead content among various lipsticks ranged from 0.026 ng mg^{-1} to 7.19 ng mg^{-1}, the mean lead concentration among 400 different lipsticks is 7.19 ng mg^{-1} [1], which seems very little but it is quite dangerous for human health even though United States Food & Drug Administration didn't determine a specific lead concentration range in cosmetics though they determined a limit in color additives in cosmetics as 20μg g^{-1} in order to prevent potential lead poisoning as a result of lead exposure from color additives. Origination of lead poisoning may also be Lead solder or leaded paint when producing the equipment or simply contaminated dust. It is approved that most color additives used in cosmetics contain Lead up to 20 μg Pb/g.

Lipstick usage is popular among women. There is no specific purpose of using lipstick, it doesn't treat anything, it only gives a good physical appearance and most women use it. Although the concentration of lead is very little in lipsticks, frequent usage increases toxic effects of lead as it accumulates in body after every use.

1.2 Methods to Determine Lead Concentration

The simplest, yet the most superficial method to determine presence of Lead in lipstick is rubbing a lipstick to a gold ring. Due to activity of metals a red-ox reactions occurs between them and gold gets darker. Even the greatest brands that are commonly used and trusted include lead and it can be simply tested by this method, not the exact amount of lead, but presence of it.

There are various methods to determine heavy metal's concentrations in cosmetic products in the literature. One of them is Zeeman Atomic Absorption Spectrophotometer with a Graphite Tube Atomizer after going through acid digestion process. Inductively coupled plasma-mass spectrometry (ICP-MS) is used to determine lead in lipsticks after microwave digestion. It was observed that X-Ray Fluorescence (XRF) was not sensitive enough to determine lead in lipsticks; it resulted with matrix absorption errors. Another technique is Laser Induced Breakdown Spectroscopy (LIBS), which is applied in Saudi Arabia. Also there is Flame Atomic Absorption Spectrometry (FAAS) to determine lead content in lipstick assisted by microwave digestion. It is seen that in all studies sample preparation included either microwave assisted acid digestion or dry ashing technique. Even so, digestion is expensive in terms of time and it causes pollution, as acid is used frequently. Also there is the risk of contamination when lipstick sample is diluted and digested in acid mixture of HNO_3 and HF, to realize this and get accurate data, a blank sample is prepared for microwave and atomic absorption spectrometer, which consists of only acid mixture from the same solutions mixed with samples in order to ascertain if there is a contamination. If so the lead concentration found in blank sample is subtracted from other lead concentration values and therefore a more accurate data is obtained. Also there can be analyte losses during digestion. Some of the analytes can remain in residue and some may stay thermally stable and it would be hard to atomize them. Per contra, another technique, direct solid sampling, could be more useful since it doesn't require preparation of sample that much. It is more sensitive than other techniques because it doesn't require dilution of sample; it is cheaper in terms of time than other techniques and risks of analyte loss and contamination is highly reduced, though it has its own disadvantages such as the amount used to determine lead concentration can be too low for whole lipstick, because lead is not spread in lipstick homogenously, the heterogeneity may result in low precision.

In this study, microwave-assisted acid digestion and atomic absorption spectrometry technique was used for the determination of lead concentration in 5 different brands of lipstick samples due to laboratory conditions and available materials. Acid digestion with the mixture of HF and HNO_3 is quite important since only one of them is not sufficient enough to solve them.

After applying the microwave-assisted solving program on samples, they were loaded in AAS. The wavelength of lead is 283.3 nm. Light from excited lead atoms, which produce the correct mixing of wavelengths to be absorbed, by any lead atoms in the sample is emitted by a light source containing lead. AAS atomizes the sample, it converts the sample into vaporized ground state free atoms and excited lead atoms passing through this sample emits a beam of electromagnetic radiation, some of this radiation is absorbed by the lead atoms in the sample. Absorption increases when there are more atoms in the vaporized sample. They are directly proportional. By loading five different brands of lipstick samples into AAS, a calibration curve is derived. The concentrations of lead in lipsticks are obtained by analyzing the curve.

1.3 Research Question

The issues with lead accumulation due to lipstick usage and effects of lead in human health led me to investigate lead concentrations in various lipsticks. Even though the results will show very small amounts and since lipstick usage is continuous, I will be able to make a guess on when will it start to be dangerous by taking critic lead concentration that human body can bear into account. So, the research question hereby is; **"How do the lead concentrations of different brands of lipstick samples solved in acid mixture and determined by using atomic absorption spectrometer vary under standard atmospheric conditions and room temperature and to what extent do they have hazardous effects?"**

1.5 Aim of the Project

Lipstick is a very popular cosmetic product that is overly used by women, and by developing industrial conditions new brands come up everyday and the competition in cosmetics grows stronger day by day. Producers lower their prices to get more customers, but this discount must be made in such a way that profit should increase or at least stay the same, and to apply this most of the brands change the quality of their ingredients, which cannot be easily spotted by ordinary customers. Those low quality ingredients usually are the ones with Lead in them because they are contaminated by industrial waste material, which makes them cheaper, and companies' desire to make more profit endangers human health by the help of unconscious consumers. Since I have lady friends, family members and teachers around me, I wanted to dispel my curiosity and warn people about this issue.

2. APPENDIX I - EXPERIMENTATION

Materials

Chemicals:

- %65 HNO_3 (105.0 mL) (±0.1)
- %38 HF (42.0 mL) (±0.1)
- Pure water (0.425 mL) (±0.001)
- 1000.0 ng/mL Lead solution (40.0 mL) (±0.1)
- **Lipsticks:**
    - Maybeline #475 Coral Diamonds
    - L'oreal #340 Sorbet Fraise Raspberry
    - Alix Avien #327
    - Golden Rose #216
    - Pastel Lipstick #400.

Figure 1. Lipsticks to be analyzed in the order given above from left to right

Equipment:

- Varian AA140 Atomic Absorption Spectrometer w/ Varian GTA 120 Graphit unit and AS-90 Plus Auto Sampler
- Biotage Initiator 2.5 Microwave Oven
- Pipettes with 5 mL and 1 mL capacity
- Plastic tubes (10 mL) (x21)
- Analytical Balance Scale (x1)
- 5cm x 5cm Paper (x20)
- Spoon Spatula (x1)
- Plastic tubes suitable for Auto Sampler (x21) (0.010 mL) (±0.001)

Safety Equipment:

- Gloves (x4)
- Laboratory Goggles (x1)
- Laboratory Coat (x1)

Variables

Independent Variable:

- Brand of lipstick

Dependent Variable:

- Lead, Pb, concentration

Controlled Variables:

- Pressure over the system (1 atm)
- Temperature of the environment (25 °C)
- Volumes of acids added to solve solid lipstick (5 mL HNO_3 and 2 mL HF)
- Microwave
- Atomic Absorption Spectrometer
- Analytical Balance Scale
- Amount of Lipstick sample added into acid mixture (0.25 g)
- Concentrations of acids (%65 HNO_3 and %38 HF)
- Pure water used to dilute Lead solution
- Amount of pure water added to lipstick samples
- Time to dissolve solutions (55 min)
- Temperature of the dissolved solutions (25.0 °C)

How to ensure controlled variables?

- Periodic controls were made when determining pressure and temperature of the system. Pressure and temperature was checked in every 20 minutes.
- The same Analytical Balance Scale was used to have more precise data even if there was a systematic error with the scale.

Procedure

1. Place a 5x5cm Paper on Analytical Balance Scale and set zero.
2. Take 0.25g sample from the lipstick using the spoon spatula and place on the paper and weigh it. Note down the data.
3. Transfer the sample into plastic tube. Rub the spoon spatula on paper, make sure to transfer all the lipstick on it to the paper.
4. Weigh the paper again and subtract the data from your initial data to acquire the net amount of lipstick in the tube.
5. Add 5 mL %65 HNO_3 into the acid-resistant tube with sample using the 5mL capacity pipette.
6. Add 2 mL %38 HF into the acid-resistant tube with sample using the 1mL capacity pipette twice.
7. Add 5 mL %65 HNO_3 and 2 mL %38 HF into a blank plastic tube as reference, to check if there is any contamination in acids.
8. Repeat steps 1-7 for 3 more times.
9. Repeat steps 1-8 for four other lipsticks.
10. Place 20 acid mixtures with lipstick and a blank sample, which contains only acid mixture, into the turning mechanism in the microwave with sealed Teflon vessels to prevent explosion. Since there are 21 samples place an empty tube into microwave to maintain its balance. Place the temperature probe into blank sample.
11. Apply the following digestion program for samples. Enter the data below to the microwave. After the digestion program is over, hold the samples in room temperature and wait until they cool down. The samples are

expected to be colorless, though there is the possibility of production of NO_2 gas, which have a brownish color, but it will fly when the tube is opened, since the experimentation was done in fume hood.

Microwave Digestion Program

Step No	Temperature (°C) (±0.1)	Time (sec) (±0.2)
1	170.0	300.0
2	190.0	1800.0
3	50.0	1200.0

Table 1. Microwave-assisted digestion program for samples.

12. If the lipstick sample can be seen in the mixture, it means that the sample is not dissolved, repeat the given microwave program. If it can't be seen, the sample is homogenously dissolved in the mixture.
13. Prepare 5mL standards with lead concentrations of 5 ng/mL, 10 ng/mL, 20 ng/mL and 50 ng/mL by diluting 1000 ng/mL Lead solution. Add 0.240ml, 0.090 mL, 0.040 mL and 0.015 mL pure water into 4 separate 10 mL of 1000 ng/mL Lead solutions respectively with the pipet. With these 4 solutions a calibration graph can be drawn and an equation can be derived which will be used to determine the Lead amounts in lipsticks in ng unit. Add 90 mL of pure water to all of the solutions with acid mixture in them, AAS is quite sensitive and high concentrations of acid can damage it, so the solutions must be diluted.

14. Place 0.01 mL of each sample in auto sampler section of the atomic absorption spectrometer in the following order, right after they cool down in aqueous state;

Placement Order of Samples in AAS

Row No	Brand of the Lipstick in the sample
1	5.0 ± 0.1 ng/mL Lead solution
2	10.0 ± 0.1 ng/mL Lead solution
3	20.0 ± 0.1 ng/mL Lead solution
4	50.0 ± 0.1 ng/mL Lead solution
5	Maybeline #475 Sample 1
6	Maybeline #475 Sample 2
7	Maybeline #475 Sample 3
8	Maybeline #475 Sample 4
9	L’oreal #340 Sample 1
10	L’oreal #340 Sample 2
11	L’oreal #340 Sample 3
12	L’oreal #340 Sample 4
13	Alix Avien #327 Sample 1
14	Alix Avien #327 Sample 2
15	Alix Avien #327 Sample 3
16	Alix Avien #327 Sample 4
17	Golden Rose #216 Sample 1
18	Golden Rose #216 Sample 2
19	Golden Rose #216 Sample 3

20	Golden Rose #216 Sample 4
21	Pastel Lipstick #400 Sample 1
22	Pastel Lipstick #400 Sample 2
23	Pastel Lipstick #400 Sample 3
24	Pastel Lipstick #400 Sample 4
25	Blank Sample

Table 2. The placement order of samples in Auto Sampler of the Atomic Absorption Spectrometer

15. By placing the mouse indicator of the computer on the peeks of the graphs of samples, a little box appears in which absorbance values can be read.
16. Since volume is 0.01 mL the first 4 rows' lead amount can easily be calculated by multiplying their volumes with their mass concentrations. The Atomic Absorption Spectrometer draws a graph according to these references which enables us to compare the absorption of unknown amount Lead in other samples with the known ones.
17. An equation will be derived from the calibration graph, such as

$$y = mx \pm a$$

in which y is the absorbent value of samples which will be read from atomic absorption spectrometer and x will be derived from this equation, which will be the amount of Lead in the samples in ng.

18. Divide the critical Pb level that body can bear to 5 times the amount of lead you found, since a lipstick weighs 5g, to obtain number of lipsticks to reach critical Pb level.

2.DATA COLLECTION

Unit Conversions;

$$\mathbf{1\ g = 10^{-6}\ \mu g = 10^{-9}\ ng}$$

Determining Mass of Lipstick

First of all, the initial amounts of lipstick samples are measured and therefore will be given. Uncertainties are the smallest value that the scale can measure.

Mass of Lipstick Samples

Brand of Lipstick	Mass of Lipstick Samples (g) (±0.0001)			
	Trial 1	Trial 2	Trial 3	Trial 4
Maybeline #475	0.2594	0.2555	0.2562	0.2573
L'oreal #340	0.2525	0.2611	0.2560	0.2542
Golden Rose #216	0.2691	0.2594	0.2543	0.2603
Alix Avien #327	0.2670	0.2601	0.2557	0.2542
Pastel #400	0.2618	0.2668	0.2574	0.2596

Table 3. Mass of initial Lipstick samples

Secondly, to acquire the net amount of sample collected, the amount of remaining sample on spoon spatula and paper must be weighed.

Mass of Lipstick Remainders

Brand of Lipstick	Mass of Remaining Lipstick Samples on Paper and Spoon Spatula (g) (±0.0001)			
	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
Maybeline #475	0.0020	0.0047	0.0035	0.0052
L'oreal #340	0.0007	0.0094	0.0034	0.0022
Golden Rose #216	0.0132	0.0012	0.0021	0.0078
Alix Avien #327	0.0115	0.0092	0.0043	0.0033
Pastel #400	0.0094	0.0113	0.0061	0.0049

Table 4. Mass of lipstick remainders on paper and spoon spatula

Finally, by subtracting the values of second table from first table, the net amount of samples will be acquired.

Maybeline #475

Trial 1;

0.2594 – 0.0020 = 0.2574 g

Trial 2;

0.2555 – 0.0047 = 0.2508 g

Trial 3;

0.2562 – 0.0035 = 0.2527 g

Trial 4;

0.2573 – 0.0052 = 0.2521 g

Uncertainty;

0.0001 + 0.0001 = 0.0002

L'oreal #340

Trial 1;

0.2525 – 0.0007 = 0.2518 g

Trial 2;

0.2611 – 0.0094= 0.2517 g

Trial 3;

0.2560 – 0.0034= 0.2526 g

Trial 4;

0.2542 – 0.0022 = 0.2526 g

Uncertainty;

0.0001 + 0.0001 = 0.0002

Golden Rose #216

Trial 1;

0.2691 – 0.0132 = 0.2559 g

Trial 2;

0.2594 – 0.0012 = 0.2582g

Trial 3;

0.2543 – 0.0021 = 0.2522 g

Trial 4;

0.2603 – 0.0078 = 0.2525 g

Uncertainty;

0.0001 + 0.0001 = 0.0002

Alix Avien #327

Trial 1;

0.2670 – 0.0115 = 0.2555 g

Trial 2;

0.2601 – 0.0092 = 0.2509 g

Trial 3;

0.2557 – 0.0043 = 0.2514 g

Trial 4;

0.2542 – 0.0033= 0.2509 g

Uncertainty;

0.0001 + 0.0001 = 0.0002

Pastel #400

Trial 1;

0.2618 – 0.0094 = 0.2524 g

Trial 2;

0.2668 – 0.0113 = 0.2555 g

Trial 3;

0.2574 – 0.0061 = 0.2513 g

Trial 4;

0.2596 – 0.0049 = 0.2547 g

Uncertainty;

0.0001 + 0.0001 = 0.0002

Net Mass of Samples

	Mass of net Lipstick Samples (g) (±0.0002)			
	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
Maybeline #475	0.2574	0.2508	0.2527	0.2521
L'oreal #340	0.2518	0.2517	0.2526	0.2526
Golden Rose #216	0.2559	0.2582	0.2522	0.2525
Alix Avien #327	0.2555	0.2509	0.2514	0.2509

Pastel #400	0.2524	0.2555	0.2513	0.2547

Table 5. Mass of net lipstick samples, found by subtracting the values from Table 4 from Table 3.

Calibration of Standards

To create a calibration graph, we need to calculate amount of Lead in reference solutions which is quite easy to find by applying;

$$Mass\ Concentration\ (\pm 0.1)\ x\ Volume(\ \pm 0.001) = Mass$$

$$\%\ Uncertainty = 100\ x\ \frac{Uncertainty}{Value}$$

Therefore here are the amounts of Lead in reference samples;

5.00 x 0.01 = 0.05ng

Uncertainty;

(0.1 / 5.0) x 100 = 2%

(0.001 / 0.01) x 100 = 10%

Total Uncertainty = 10 + 2

Total Uncertainty = 12%

Uncertainty = 0.006

10.00 x 0.01 = 0.10ng

Uncertainty;

(0.1 / 10.0) x 100 = 1%

(0.001 / 0.01) x 100 = 10%

Total Uncertainty = 10 + 1

Total Uncertainty = 11%

Uncertainty = 0.011

20.00 x 0.01 = 0.20ng

Uncertainty;

(0.1 / 20.0) x 100 = 0.5%

(0.001 / 0.01) x 100 = 10%

Total Uncertainty = 10 + 0.5

Total Uncertainty = 10.5%

Uncertainty = 0.021

50.00 x 0.01 = 0.50ng

Uncertainty;

(0.1 / 50.0) x 100 = 0.2%

(0.001 / 0.01) x 100 = 10%

Total Uncertainty = 10 + 0.2

Total Uncertainty = 10.2%

Uncertainty = 0.051

Mass of Lead and their Absorbance

Mass of Lead (ng)	Absorbance (nm) (±0.0001)
0.050 (±0.006)	0.0474

0.100 (±0.011)	0.0850
0.200 (±0.021)	0.1512
0.500 (±0.051)	0.4443

Table 6. Mass of Lead in Standards and their Absorbance read from AAS

So the calibration graph is;

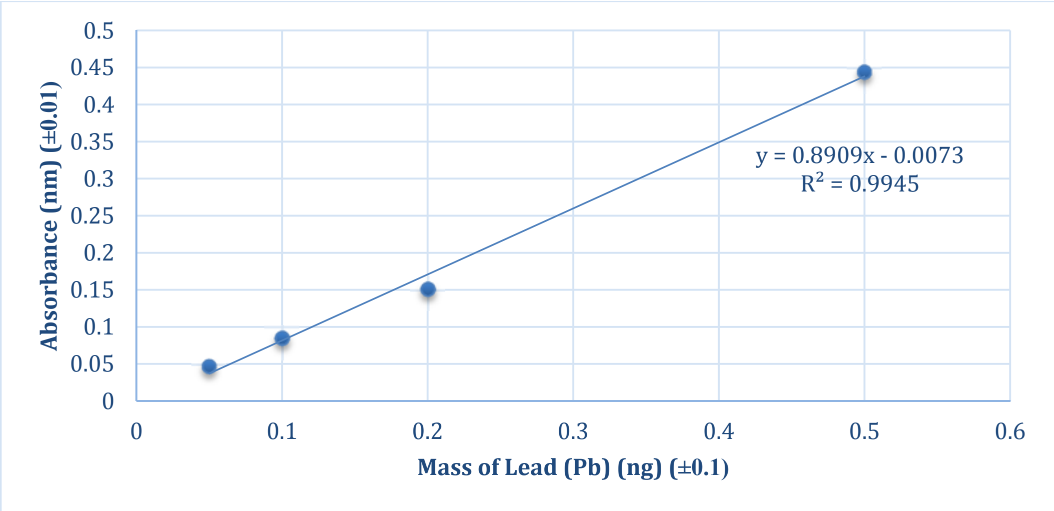

Figure 2. The Calibration Graph formed by using the absorbance values of standards, with the derived equation.

The equation is derived from the graph which is;

$$y = 0.8909x - 0.0073$$

where y is the absorbent values of samples and the calculated x will be the amount of Lead in lipsticks in ng.

Absorbance of Samples

To use the formula we first need absorbent values of the samples.

Absorbent values of Samples

Brand of Lipstick	Absorbent values Lipstick Samples (nm) (±0.0001)			
	Trial 1	Trial 2	Trial 3	Trial 4
Maybeline #475	0.0934	0.0884	0.0912	0.0903
L'oreal #340	0.0873	0.0.823	0.0834	0.0867
Golden Rose #216	0.1223	0.1262	0.1244	0.1219
Alix Avien #327	0.0953	0.0895	0.0921	0.0899
Pastel #400	0.1450	0.1473	0.1426	0.1412

Table 7. Absorbent values of samples read from Atomic Absorption Spectrometer.

Blank Sample's absorbent value was 0.0007, even though it is very small, it still indicates that there was a little contamination. Though it can be ignored since it doesn't have a major significant effect.

Average Absorbent values are calculated to have accurate results;

Maybeline #475

(0.0934 + 0.0884 + 0.0912 + 0.0903) / 4 = 0.0908

Uncertainty (by Standard Deviation)

(0.0934 – 0.0884)/4 = 0.0012

L'oreal #340

(0.0873 + 0.0.823 + 0.0834 + 0.0867) / 4 = 0.0849

Uncertainty (by Standard Deviation)

(0.0873 – 0.0823)/4 = 0.0012

Golden Rose #216

(0.1223 + 0.1262 + 0.1244 + 0.1219) / 4 = 0.1237

Uncertainty (by Standard Deviation)

(0.1262 – 0.1219)/4 = 0.0011

Alix Avien #327

(0.0953 + 0.0895 + 0.0921 + 0.0899) / 4 = 0.0917

Uncertainty (by Standard Deviation)

(0.0953 – 0.0895)/4 = 0.0014

Pastel #400

(0.1450 + 0.1473 + 0.1426 + 0.1412) / 4 = 0.1440

Uncertainty (by Standard Deviation)

(0.1473 – 0.1412)/4 = 0.0015

Average Absorbent values of Samples

Brand of Lipstick	Average Absorbent values Lipstick Samples (nm)
Maybeline #475	0.0908 ± 0.0012
L'oreal #340	0.0849 ± 0.0012
Golden Rose #216	0.1237 ± 0.0011
Alix Avien #327	0.0917 ± 0.0014
Pastel #400	0.1440 ± 0.0015

Table 8. The average absorbent values of the samples, found by summing values from Table 6 and dividing the result to 4 for each sample.

Amount of Lead found in 1 g of Lipstick

Applying the formula for approximately 0.25g sample;

$$y = 0.8909x - 0.0073$$

The uncertainty will be the same since there is no uncertainty in any other element of the equation.

Maybeline #475;

0.0908 = 0.8909x – 0.0073

x = 0.1101 ± 0.0012 ng

L'oreal #340

0.0849 = 0.8909x – 0.0073

x = 0.1035 ± 0.0012 ng

Golden Rose #216

0,1237 = 0.8909x – 0.0073

x = 0.1470 ± 0.0012 ng

Alix Avien #327

0,0917 = 0.8909x – 0.0073

x = 0.1111 ± 0.0012 ng

Pastel #400

0,1440 = 0.8909x – 0.0073

x = 0.1698 ± 0.0012 ng

Mass of Lead in Samples

Brand of Lipstick	Mass of Lead in Lipstick Samples (ng)
Maybeline #475	0.1101 ± 0.0012
L'oreal #340	0.1035 ± 0.0012
Golden Rose #216	0.1470 ± 0.0011
Alix Avien #327	0.1111 ± 0.0014
Pastel #400	0.1698 ± 0.0015

Table 9. Mass of Lead in Lipstick samples derived from Calibration Graph's formula

The average masses of samples are needed to calculate mass of Lead in 1g lipstick.

Maybeline #475

(0.2574 + 0.2508 + 0.2527 + 0.2521) / 4 = 0.2532

Uncertainty (by Standard Deviation)

(0.2574 – 0.2508)/4 = 0.0017

L'oreal #340

(0.2518 + 0.2517 + 0.2526 + 0.2526) / 4 = 0.2522

Uncertainty (by Standard Deviation)

(0.2526 – 0.2517)/4 = 0.0002

Golden Rose #216

(0.2559 + 0.2582 + 0.2522 + 0.2525) / 4 = 0.2547

Uncertainty (by Standard Deviation)

(0.2582 – 0.2522)/4 = 0.0015

Alix Avien #327

(0.2555 + 0.2509 + 0.2514 + 0.2519) / 4 = 0.2522

Uncertainty (by Standard Deviation)

(0.2555– 0.2509)/4 = 0.0012

Pastel #400

(0.2524 + 0.2555 + 0.2513 + 0.2547) / 4 = 0.2535

Uncertainty (by Standard Deviation)

(0.2555 – 0.2513)/4 = 0.0010

Average mass of net Samples

	Average Mass of net Lipstick Samples (g)
Maybeline #475	0.2532 ± 0.0017
L'oreal #340	0.2522 ± 0.0002
Golden Rose #216	0.2547 ± 0.0015
Alix Avien #327	0.2522 ± 0.0012
Pastel #400	0.2535 ± 0.0010

Table 10. Average mass of the Lipstick samples, calculated by summing values of Table 5 and dividing the result to 4 for each sample.

A simple ratio relation will give us the amount of Lead in 1g of lipstick in ng;

$$y = \frac{Mass\ of\ Lead\ found\ in\ Sample}{Mass\ of\ Sample}$$

Maybeline #475;

y = (0.1101) / (0.2532)

y = 0.4348 ng

L'oreal #340

y = (0.1035) / (0.2522)

y = 0.4104 ng

Golden Rose #216

y = (0.1470) / (0.2547)

y = 0.5771 ng

Alix Avien #327

y = (0.1111) / (0.2522)

y = 0.4405 ng

Pastel #400

y = (0.1698) / (0.2535)

y = 0.6698 ng

Uncertainties;

The uncertainty can be found with;

$$Max\ y = \frac{Max\ Mass\ of\ Lead\ found\ in\ Sample}{Max\ Mass\ of\ Sample}$$

$$Min\ y = \frac{Min\ Mass\ of\ Lead\ found\ in\ Sample}{Min\ Mass\ of\ Sample}$$

$$Uncertainty = \frac{Max\ y - Min\ y}{2}$$

Maybeline #475;

Max;

0.1113 / 0.2549 = 0.4366

Min;

0.1089 / 0.2515 = 0.4330

Uncertainty = (0.4366 – 0.4330) / 2

Uncertainty = 0.0018

L'oreal #340;

Max;

0.1047 / 0.2524 = 0.4148

Min;

0.1023 / 0.2520 = 0.4060

Uncertainty = (0.4148 – 0.4060) / 2

Uncertainty = 0.0044

Golden Rose #216;

Max;

0.1481 / 0.2562 = 0.5781

Min;

0.1459 / 0.2532 = 0.5762

Uncertainty = (0.5781 – 0.5762) / 2

Uncertainty = 0.0010

Alix Avien #327;

Max;

0.1125 / 0.2534 = 0.4440

Min;

0.1097 / 0.2510 = 0.4370

Uncertainty = (0.4440 – 0.4370) / 2

Uncertainty = 0.0035

Pastel #400;

Max;

0.1713 / 0.2545 = 0.6731

Min;

0.1683 / 0.2525 = 0.6665

Uncertainty = (0.6731 – 0.6665) / 2

Uncertainty = 0.0033

Mass of Lead in 1g Sample

Brand of Lipstick	Mass of Lead in 1g Lipstick Samples (ng/g)
Maybeline #475	0.4348 ± 0.0018
L'oreal #340	0.4104 ± 0.0044
Golden Rose #216	0.5771 ± 0.0010
Alix Avien #327	0.4405 ± 0.0035
Pastel #400	0.6698 ± 0.0033

Table 11. Amount of Lead found in 1g of Lipstick.

Qualitative Data

- L'oreal and Golden Rose samples were colorless at the beginning, after microwave digestion their color turned into something like blue and green. Other samples remained colorless.
- When the tube is opened a brown gas, probably NO_2, came out.
- The brown gas had a sharp scent.
- High concentrations of HF has a scent, since the inhalation of HF is hazardous, I used it under fume cupboard so I wasn't able to smell any of the acids.

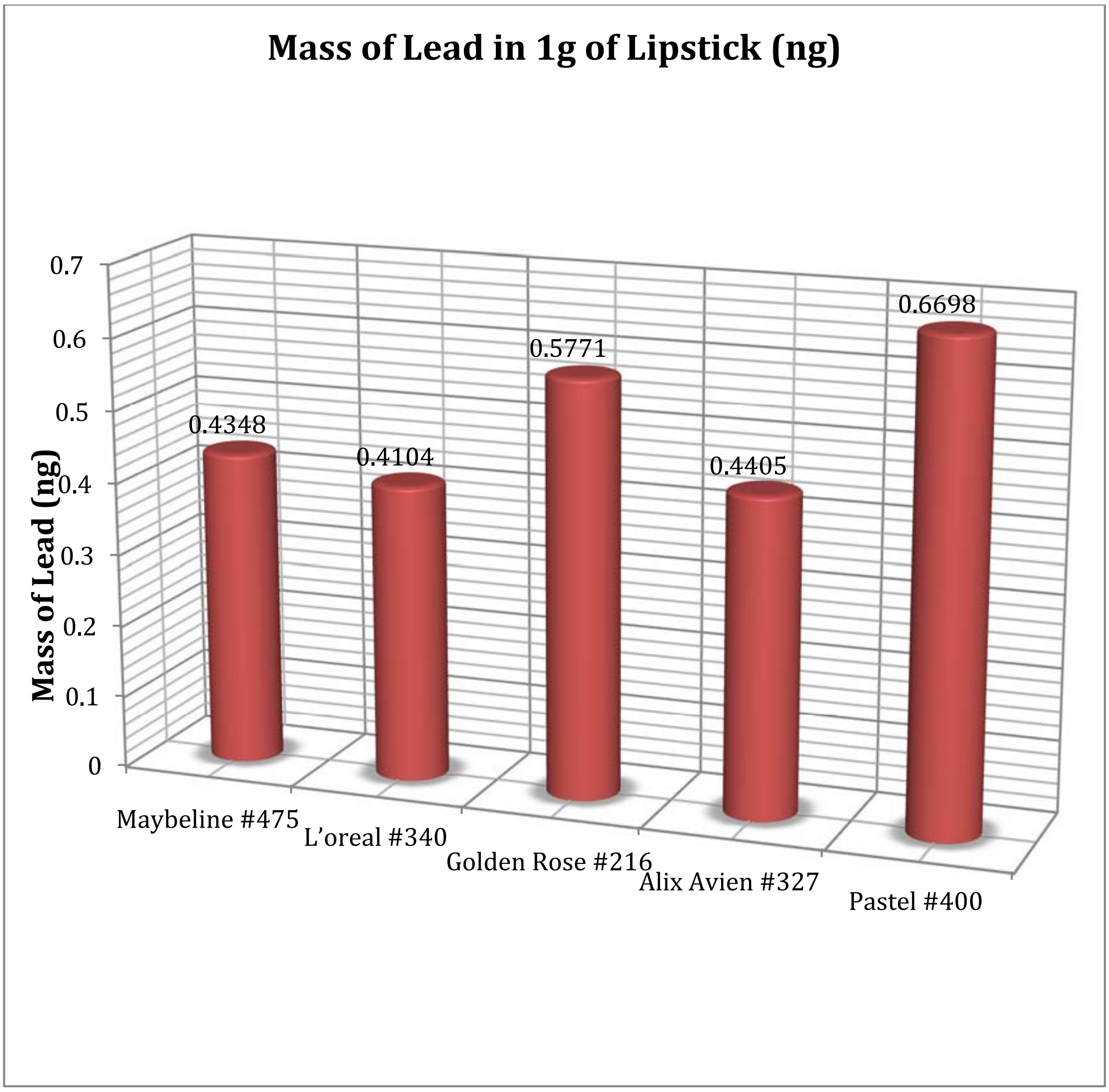

Figure 3. The graph of amount of Lead found in 1g of Lipstick sample in ng

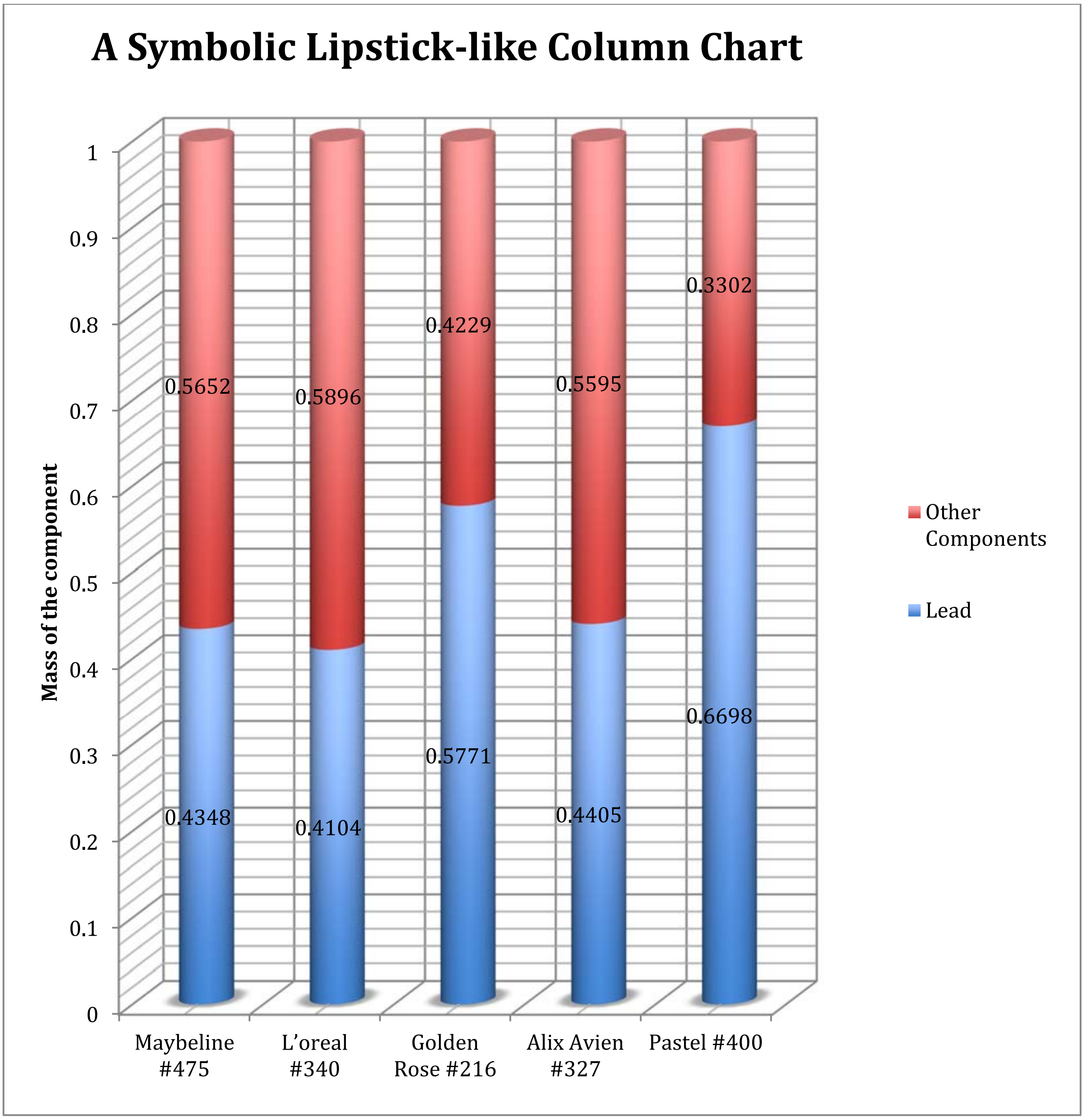

Figure 4. A symbolic chart showing the MAXIMUM amount of Lead in 1g of Lipstick. (The chart shows 1 ng of lipstick sample and it is assumed that all the Lead content is in this 1 ng section, so blue series are the maximum amount of Lead, so when the values on blue series are multiplied with 10^{-6} the result shows the amount of Lead in 1g Lipstick in terms of g.)

Critical Number of Lipsticks

The Centers for Disease Control set the critic Lead level for adults as 10.0 μg/dl and it is much lower, 5.0 μg/dl, for children, since they have less developed immune system and more fragile it makes them more vulnerable than adults. 10 μg/dl is equal to 100.0 ng/mL. Usually the standard mass of lipstick is 5g and our values are calculated according to 1 g of lipstick, therefore they are multiplied by 5. The number of lipsticks required to reach critical level, for adults, can be easily calculated by;

$$Number\ of\ Lipstick\ required = \frac{Concentration\ of\ Critical\ \text{Level}\ (\pm 0.1)}{5\ x\ Concentration\ of\ Lead\ in\ Lipstick}$$

$$\%\ Uncertainty = 100\ x\ \frac{Uncertainty}{Value}$$

Maybeline #475;

100 / (0.4348 x 5) = 46 Lipsticks

Uncertainty;

(0.1 / 100.0) x 100 = 0.1%

(0.0018 / 0.4348) x 100 = 0.4%

Total Uncertainty = 0.1 + 0.4

Total Uncertainty = 0.5%

Uncertainty = 0.2

L'oreal #340;

100 / (0.4104 x 5) = 49 Lipsticks

Uncertainty;

(0.1 / 100.0) x 100 = 0.1%

(0.0044 / 0.4104) x 100 = 1.0%

Total Uncertainty = 0.1 + 1.0

Total Uncertainty = 1.1%

Uncertainty = 0.5

Golden Rose #216

100 / (0. 5771 x 5) = 35 Lipsticks

Uncertainty;

(0.1 / 100.0) x 100 = 0.1%

(0.0010 / 0.5771) x 100 = 0.2%

Total Uncertainty = 0.1 + 0.2

Total Uncertainty = 0.3%

Uncertainty = 0.1

Alix Avien #327

100 / (0.4405 x 5) = 46 Lipsticks

Uncertainty;

(0.1 / 100.0) x 100 = 0.1%

(0.0035 / 0.4405) x 100 = 0.8%

Total Uncertainty = 0.1 + 0.8

Total Uncertainty = 0.9%

Uncertainty = 0.4

Pastel #400

100 / (0.6698 x 5) = 30 Lipsticks

Uncertainty;

(0.1 / 100.0) x 100 = 0.1%

(0.0033 / 0.6698) x 100 = 0.5%

Total Uncertainty = 0.1 + 0.5

Total Uncertainty = 0.6%

Uncertainty = 0.2

Number of Lipsticks for Critic Level

Name of the Lipstick	Number of Lipsticks for Critic Level
Maybeline #475	46.0 ± 0.2
L'oreal #340	49.0 ± 0.5
Golden Rose #216	35.0 ± 0.1
Alix Avien #327	46.0 ± 0.4
Pastel #400	30.0 ± 0.2

Table 12. The number of lipsticks required to reach critical level.

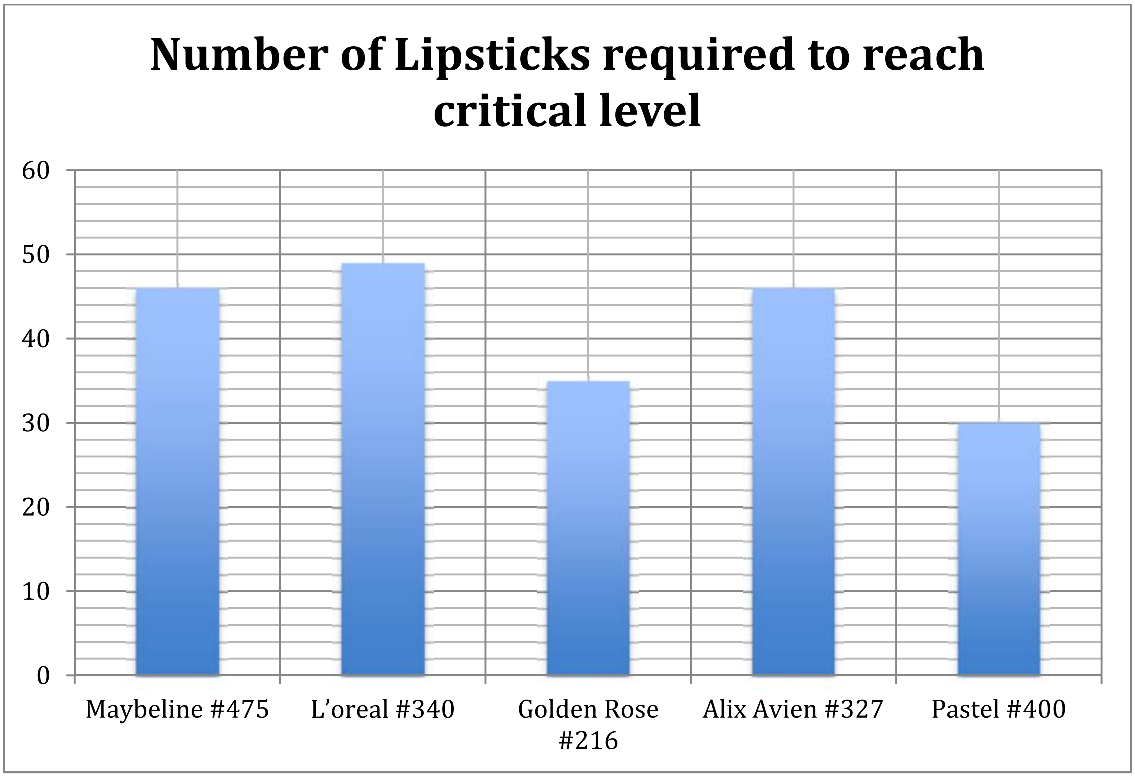

Figure 5. The number of lipsticks required to reach critical level.

As it can be read from the column graph, the most dangerous lipstick among these is Pastel, since it requires less usage, about 30 lipsticks, to reach critical Lead level. Golden Rose comes right after it with usage of 35 lipsticks to reach critical level. There is a huge gap between these two and the other three. Maybeline, L'oreal and Alix Avien have quite close values; 46, 49 and 46 respectively, so they are less dangerous than Pastel and Golden Rose, but still though this won't change the effectiveness of Lead in them but time to reach the critical level. Along with this, other cosmetic products, such as eyeliner, eye shadow and mascara, also include lead in them and since most of the cosmetic products are used together, the critical lead level will be reached when less number of lipsticks given above is used.

3. CONCLUSION AND EVALUATION

In this study a topical issue, Lead concentration in Lipsticks, was investigated. Lead is found in lipsticks due to their ingredients such as waxes, polishes, emollients, oils, antioxidants, dye pigments and filling materials like silica, mica, titanium dioxide and fish scales. Since the Lead is in very small amounts, atomic absorption spectrometer was used to determine the amount of lead in sample. The Atomic Absorption Spectrometer used in the investigation didn't have a furnace and since the acid mixture of 5 mL HNO_3 and 2 mL HF is not sufficient enough to solve solid lipstick sample, the digestion process was assisted by a microwave ran in a specific program. Obtained results showed that, as expected, all of the samples contained Lead in them, even though it is in small amounts. AAS determines the wavelengths of absorbed rays from standards with known concentrations and compares the absorption of samples with them to find unknown lead concentrations.

The values of Lead amount in Maybeline, L'oreal and Alix Avien are pretty close to each other, still though Pastel Lipstick stood out as the most risky one since it has the greatest amount of lead in 1 g of it. The relation between them is;

$$Pastel\ > Golden\ Rose\ > Alix\ Avien\ > Maybeline\ > L'oreal$$

since Pastel contains 0.6698 ng Lead with %0.41 uncertainty, Golden Rose contains 0.5771 ng Lead with %1.07 uncertainty, Alix Avien contains 0.4405 ng Lead with %0.17 uncertainty, Maybeline contains 0.4348 ng Lead with %0.79

uncertainty and L'oreal contains 0.4104 ng Lead with %0.49 uncertainty in 1 g of Lipstick.

Perpetual low-level intakes of heavy metals, such as Lead, have hazardous effects on human body, since there is no developed mechanism in the body to eliminate heavy metals. Lead is a cumulative poison and it accumulates in body and starts to show its effects when it reaches a critical level, since it is exceptionally toxic. As calculated in Data Collection section, after using 30 lipsticks, the accumulated lead starts to show its effects. The effect of lead poisoning in body changes according to amount of lead accumulated and strength of immune system. Even though the body is unable to eliminate them, a strong immune system can delay the hazardous effects of lead. Lead damages wherever it lands in body since it is carried like a mineral and distributed to everywhere.

The hardest part of the experiment was microwave digestion phase. Actually it is quite easy to use the microwave, set the digestion program and install the samples in sealed Teflon vessels, though there was a systematic problem with the microwave, it couldn't apply the program and won't heat the given solutions so until it was renewed, the experiment was postponed.

Evaluation of the Method

The technique used to determine amounts of Lead in lipstick samples is expensive in terms of both time and money. To have more accurate data, paper is used while taking 0.25 g sample, to find the net amount of sample, which will be closer to the exact value, and that process took around 30-35 minutes, since there were 20 samples. Preparing the acid mixture was the easiest, pipets with adjustable capacity allowed us to finish this phase in about 5 minutes. Due to available equipment digestion was assisted by a microwave. At the first day in the laboratory, a problem came up with the microwave, it gave a systematic failure and the microwave didn't start, so the program couldn't be applied. After the microwave in Analytical Chemistry Department was renewed, the digestion program become available to apply. It took 55 minutes and the samples needed at least 40 minutes to cool down to room temperature, 25.0 °C. As far as I observed, there were no precipitation after the samples cooled down, so the probability of high amount of Lead that didn't dissolve in the acid mixture is quite low. The applied technique, which involved atomic absorption spectrometer, is quite sensitive since it measures very low heavy metal concentrations. A strong acid HNO_3 was used during digestion phase and since AAS is sensitive, the solutions needed to be diluted by pure water. However, working with dilute solutions increases the probability of error and there is always the risk of contamination. The contamination can be because of using not completely pure water, water with some minerals and heavy metals in it, or it can be because of mixing a solution with lead in it with either pure water or acids earlier. This can be dealt by using standard solutions instead while using AAS and forming calibration graph, also using low concentrations of acids during the digestion process can dispel the need for dilution.

Surprisingly, the blank sample, acid mixture only, created a peek when placed in the AAS, which indicated that there is lead in it. Though the peek is so small when compared to the standards and it could be neglected, since it doesn't have a significant effect on any of the samples. Still though, there is contamination and it could be both systematic error and random error. The little tube at the tip of pipet should be changed after every use to prevent contamination, this detail could have eluded observation and cause contamination. The systematic error probability in this contamination issue can be dealt by diluting half of the four trials belonging to the same sample with another pure water, and/or adding acids from another flask with the same concentration. The random error probability can be dealt by using 21 different pipets, which is quite insensate, or simply the experimenter can be scrupulous about changing the tube at the tip after every use. Uncertainties were quite low when compared to the original values. The converted percentage uncertainties indicate that the experiment didn't involve much systematic error since they were between 8-12% range.

There is the probability of occurrence of side reactions in L'oreal and Golden Rose samples, because unlike other samples a brown gas, NO_2 probably, came out when the tube is opened and the solutions were greenish until they were diluted, as soon as pure water was added to the greenish solutions their colors became colorless again. This mean that there were at least 2 side reactions, one with NO_2 product and color change and the other with only color change. This side reactions may cause a loss in net amount of Lead since one of them had a product which was in gaseous state and released when the tube is opened. Colorless gaseous state complexes could have been formed and released when the tube is opened and due to that, there can be loss in Lead amount in those two brands' samples. A possible reaction between HNO_3 and a compound resulted in formation of NO_2 gas in some of the samples, which might have taken some lead with it when it was released in the fume hood.

The homogeneities of the lipsticks are also unknown. The samples are taken from the top of lipstick, even though the lipstick is in solid state, heavy metals could have been deposited at the end of lipstick as a result of gravitational force. This issue can be dealt by solving whole lipstick, though it would be expensive in terms of both time and money, since larger amount of acid mixtures will be needed and the time of digestion will be longer.

Another way to deal with errors is using an alternative way to carry out the experiment. An alternative method can be used, by using different equipment. Microwave-digestion phase can be skipped by using Solid Sampling High Resolution Continuum Source Electro Thermal Atomic Absorption Spectrometry. (SS HR CS ET AAS.) SS HR CS ET AAS uses a different program, which involves drying, pyrolysis, gas adaption, atomization and cleaning stages and all of the phases done in this experiment are done in a single machine.

The experiment was carried out in room temperature, the samples wouldn't be affected even there was a change in room temperature but the calibration of standards can be affected by this change and eventually result in errors in the data.

Lipsticks are made up of fats, pigments, dyes, minerals, some reference materials such as coal, wear metals in oil, organic Lead in oil, milk powder and estuarine sediment can be analyzed. Nitric acid, HNO_3, acid digestion can complete recover Lead from all of these references except for the one with mineral content, estuarine sediment. A complete recovery of lead with the exception can be dealt with addition of hydrofluoric acid, HF, and excess boric acid, H_3BO_3 , to neutralize hydrofluoric acid and to dissolve insoluble fluorides. Since there were no boric acid in the laboratory, the experiment was carried out without neutralization phase.

Preparation of the samples were done on the same day, microwave-assisted acid digestion and atomic absorption spectrometer phase was done on another day.

Further Investigation

The data collected indicated that all of the lipsticks used in the experiment contained Lead even they were in small concentrations. It is still risky since heavy metals like lead are cumulative. They can accumulate in the body until they reach a critical level and start to show off their effects on human body, which is hazardous and rough to treat.

Apart from the fact that the companies won't tell the lead concentration in their products, they use risky ingredients to lower their prices and win a high place in the competition by making more profit. If a company lower its prices by using low-grade ingredients their sale will increase because of unconscious consumers, and other companies will apply the same strategy, which will eventually lower the quality of the market and even if they don't realize lower their profit according to the Prisoner's Dilemma. States can enact legislations in order to bind companies to the law to make them clearly state the ingredients and their contents with their quantities.

The containment of lead in lipstick can be easily determined without a lab. Due to activity of metals, when a 24-14 carat golden accessory is rubbed to lipstick, it changes color. The lipstick becomes darker, a color between grey and black, because lead is more active than gold. This is an easy method which can be done by almost everyone who uses lipsticks. Before using a lipstick this simple test can be done, to prevent lead poisoning and gaining awareness and becoming conscious on companies' products.

The data collected from this investigation can't be compared with the literature value, since no company would announce the amount of lead in their products, even they don't warn people that there is lead in their products. Though there is a similar investigation done in Istanbul Technical University by Prof. Dr. Suleyman Akman and Research Assistant Sema Gunduz, but still they didn't give the brands of the lipsticks, instead they labeled them as Lipstick 1, Lipstick 2 etc. Though, by contacting the experimenters, common lipsticks that are used can be identified and can be used to calculate percentage error and make a genereal comparison between the samples.

Furthermore, I would like to move along on this topic in potential universities I would like to study in, METU, Bilkent, Koc and ITU. I would like to collect new data with other possible methods to determine lead concentration in lipsticks. By comparing the data of each different method, I can achieve more accurate data and test the reliability of each method.

All in all, this investigation confirmed that some of the lipsticks in the market contain Lead in them and since lipstick usage is a chronic habit, the Lead accumulated in the body will reach critical levels eventually. Either the manufacturers should increase the quality of their products and be more careful while choosing their materials, or the consumers should become more conscious and stop buying risky products for human health and even for the future world. Especially products like lipstick, which doesn't supply any benefit other than nice physical appearance and doesn't cure anything, besides poison human body, should be manufactured and consumed consciously, because health is hard to gain once it is lost.

BIBLIOGRAPHY

1. Suleyman Akman, Sema Gunduz, Istanbul Technical University, Investigation of lead contents in lipsticks by solid sampling high resolution continuum source electrothermal atomic absorption spectrometry, 2012.
2. Harvard Health Publications, Lead Poisoning. (http://www.drugs.com/health-guide/lead-poisoning.html)
3. Mayo Clinic Staff, Lead Poisoning. (http://www.mayoclinic.org/diseases-conditions/lead-poisoning/basics/definition/con-20035487)
4. Pranay Kathuria, MD, FACP, FASN, FNKF, Lead Toxicity Treatment & Management, 2014.
5. Woolf AD, Goldman R, Bellinger DC. Update on the clinical management of childhood lead poisoning. Pediatr Clin North Am. 2007; 54:271-294.
6. "Lead Poisoning" Eric Perez, MD, St. Luke's / Roosevelt Hospital Center, NY, NY, and Pegasus Emergency Group (Meadowlands and Hunterdon Medical Centers), NJ. VeriMed Healthcare Network. Also reviewed by A.D.A.M. Health Solutions, Ebix, Inc., David Zieve, MD, MHA, Bethanne Black, Stephanie Slon, and Nissi Wang. (http://www.nlm.nih.gov/medlineplus/ency/article/002473.htm)
7. Tom Morris, Dawn Petinelli, Don't Eat Your Vegetables, 2007
8. Amy J. Pearse, Mary C. Mitchell, Nutrition and Childhood Lead Poisoning, Ohio (http://ohioline.osu.edu/hyg-fact/5000/5536.html)

9. Kathy B. and Julia W. from American Baby, Lead Exposure 101.
10. Sanaa Shanab, Ashraf Essa and Emad Shalaby, Bioremoval capacity of three heavy metals by some microalgae species (Egyptian Isolates)
11. Förnster U, Salamons W., Mader P., Heavy Metals, 1995.
12. UNEP/PGA Coordination Office, Heavy Metals, 2004. (http://oceansatlas.org/unatlas/uses/unepstextsph/wastesph/2602gpa.html)
13. Bianchi V., Gauglhofer J, Metals and their compounds in the environment. NY, VCH Publisher, 1991.
14. CRC Handbook of Chemistry and Physics, 64th edition, CRC Press Inc., 1984.
15. Bernhald Welz, Michael Sperling, Atomic Absorption Spectrometry, 3rd edition, Wiley-VCH
16. Hande Gurer, Nuran Ercan, Turkey, Can antioxidants be beneficial in the treatment of lead poisoning?
17. E. Rice Morgan, Treatment of Lead Poisoning, 1900
18. Tracy Fernandez Rysavy, Why is toxic lead in lipstick, 2013
19. "A Poison Kiss: The Problem of Lead in Lipstick," (http://www.safecosmetics.org/your_health/poisonkiss.cfm)
20. Nancy M. Hepp, William R. Mindak and John Cheng, Office of Cosmetics and Colors (N.M.H) and Office of Regulatory Science (W.R.M., J.C.), Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, College Park, MD 20740.