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Heavy Metal Determination in Lipstick Products Using Inductively Coupled Plasma (ICP)

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Cosmetics production and use are growing worldwide, yet users are concerned about toxicity and heavy metal pollution. Following nitric acid digestion, the estimated levels of lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), titanium (Ti), iron (Fe), and cobalt (Co), in 6 brands of lipstick (12 samples) obtained in the Saudi market have been computed by inductively coupled plasma optical emission spectroscopy. Correlation coefficients (R2) varied from 0.9992 to 0.9999 on the calibration curve, indicating good linearity. Except for low-cost specimens, the findings indicate that the concentrations of the metals under investigation are often lower than the acceptable limits of both the Saudi Standards, Metrology, and Quality Organization (SASO) and the Food and Drug Administration (FDA) (which revealed the maximum lead levels of 125.30 ppm, exceeding the allowed limit of 10 ppm). Arsenic was discovered in significant concentrations, exceeding the SASO permitted limit. Nickel was found at the FDAs allowable limit; chromium and cobalt were found in variable quantities in the majority of the specimens. Dark-colored lipstick had a greater overall content of heavy metals than light-colored lipstick. Numerous tests on SASO-approved lipsticks were conducted as part of the research. The lower-cost specimens were of

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lesser quality, failing some SASO tests. All such findings suggest that users should be cautious when buying low lipsticks since heavy metals may build up in the body over time, causing skin problems or diseases like cancer.

Keywords: Heavy metals; cosmetic products; lipsticks; biological effects; ICP-OES.

1. INTRODUCTION

Cosmetics and personal care products have played an essential role for thousands of years. Cosmetics are discarded in excess of $40 million a year all over the world. Every year, Saudi Arabian and Arabic women pay 4 billion riyals on cosmetics, oblivious to the fact that such items can include toxic chemicals and hazardous metals that could harm their health if utilized incorrectly [1]. Lip makeup is mostly used by women to accentuate their femininity and attractiveness [2]. Waxes, butter, fats, oils, hydrocarbons, and pigments for color are all used in lipstick. Lipsticks may also include flavors and perfumes, as well as ingredients that provide ultraviolet (UV) protection and plumping effects [3]. A huge number of heavy metals are utilized as colouring agents or included as deliberate ingredients in lipstick. Some, on the other hand, are unintentionally added from the atmosphere [4]. In comparison to other cosmetics, lipstick has traditionally had less negative effects.

Numerous studies on cosmetics, notably lipstick, have been carried out in order to measure the levels of heavy metal contamination. Piccinini et al. [5] investigate 223 lipstick and lip-gloss specimens in three price levels. According to the results, lead was found in 49 specimens (22%) with a ratio larger than 1 mg/kg, accounting for 4% of the lip glosses and 31% of the lipsticks examined. They additionally discovered that lipsticks had a lead concentration of (0.75 mg/kg), which was approximately double that of lip glosses (0.38mg/kg). Furthermore, the researchers established that the difference is statistically significant with a 95% probability. Another study indicates that the optimization and validation of the ICP-OES method permitted an accurate and precise determination of Al, Cd, Cr, Co, Cu, Ni, Pb, Fe, Sb, Mn, and Zn in lipstick [6]. In addition, ICP-MS instrument was used to determine some elements, which have toxicological properties (As, Cd, Co, Cr, Cu, Ni, and Pb) in homemade traditional cosmetic products including lipstick, and give very accurate and precise results [7]. Using ICP-MS and the Cold Vapour Atomic Fluorescence Spectrometer, the overall amount of 7 potentially toxic elements in 150 cosmetic goods of 12 different types, included lipsticks, was investigated. 3.1 mg/kg Cr, 0.21 mg/kg As, 0.85 mg/kg Pb, 0.91 mg/kg Co, and 2.7 mg/kg Ni were the median heavy metal concentrations in cosmetic items. Hg and Cd, on the other hand, were determined to be below detection limits [8]. In 2016, a Saudi study was conducted with the aim of quantifying the quantities of the heavy metals Pb, Cd, Hg, and As in lipstick products. In the Riyadh market, there are a total of 21 famous brands of lipstick. The Hg concentration was the greatest, followed by As and Cd, while Pb was the lowest. The findings show that all of the samples had toxic heavy metal levels below those set by the US Food and Drug Administration. There was no significant variance between lipsticks in various price categories [9].

This study aimed to examine the quality control of some lipstick products that sell in the Saudi Arabia market. Many experiments were used to assess the lipstick quality, as per the SASO 1872/201010 standard: visual investigation, rancidity (peroxide number), microbiological evaluation, a softening point test, the particle size of undispersed pigments, and identification of toxic heavy metals (Pb, As, Hg, and Cd). Other tests to be carried out include pH measurements, metal detection (zn, Cr, Co, Ni, and Ti), and calculating TiO_2 and ZnO percentages present.

2. EXPERIMENTAL

2.1 Questionnaire

Conducting a statistical study on 226 Saudi women in Saudi society to choose the lipsticks understudy, establish their level of understanding about the usage of lipstick, as well as the potential harm that utilizing it could cause.

2.2 Sample Collection

There are many lipstick brands available in Saudi markets. There are several source countries, quality levels, and pricing options available. Twelve lipsticks were selected depending on the findings of the questionnaire (which was done on 226 women). The lipsticks were priced between

5 and 159 SR (1.33 and 42.38$). The lipsticks were divided into 3 groups: low-cost (brands 1 and 2), medium-cost (brands 3 and 4), and expensive (brands 5 and 6). Each brand has 2 different colors, one dark and the other light. There are a total of 12 samples from different sources: Thailand, United Arab Emirates, Italy, Belgium, and France. The samples were collected during 2019-2020.

2.3 SASO Lipstick Testing Experiments

Lipsticks are subjected to numerous qualitative and quantitative tests to ensure that they are safe before being released on the market.

Visual inspection: Lipstick samples must be visually evaluated with the naked eye to determine that the product is in conformity in regards of color, smell, and structure [10].

2.3.1 Rancidity (peroxide number)

A peroxide number test is used to ensure that cosmetic products are of good quality, particularly when it comes to vegetable oils as well as other rancidity-prone materials that are regularly employed in colorless lipstick base mixes. Rancidity (peroxide number), max is 10 for lipsticks according to SASO 1871/2009. **Procedure**: In a 250 mL conical flask, weigh 5.0 ± 0.05 g of lipstick and dissolve in 30 mL of an acetic acid - chloroform mixture (3:2). To dissolve the sample, heat if necessary. 0.5 ml saturated potassium iodide (KI) solution, newly produced. Following 2 minutes of shaking, add 30 mL distilled water and titrate with 0.01 N sodium thiosulfate solution, employing starch as an indicator [10].

2.3.2 Microbiological examination

Because of the impurity of microorganisms, product spoilage occurs, and when customers come into touch with those pathogens, a major health risk exists. Lipstick contains a maximum of 100 microorganisms per gram [11]. **Procedure:** Following isolation from the sample, the plates have been incubated at 37°C for 24 hours to evaluate the number of bacteria contained in the sample in Petri dishes. Researchers used an Interscience Scan 500 colony counter to assess the visible colonies. They also measured bacterial colonies in CFU/ml and compared them to the control [10].

2.3.3 Softening point test

The softening point is the temp at which a material is softer before reaching some arbitrary softness. This test is used to determine the stability of lipstick at high temps. As per national standards, lipsticks minimum softening point ought to be 55°C [11]. **Procedure:**

In a flat bottom tube, put the lipstick with the protruding salve. Fix the thermometer with a cork so that the thermometers bulb is just touching the lipstick salve. Put this arrangement one centimeter over the top of the lipstick salve in 1 litre beaker filled with water. Slowly heat the water to a temperature of no more than 20°C / min, stirring occasionally. Increase the temp at a rate of 10oC/min once it reaches around 45oC. Constantly watch the lipstick salve. Record the temperature when the salve starts bending and losing its shape [10].

2.3.4 Undispersed pigment particle size

This test detects the existence of undesirable solid particles in lipstick. This is an important test since regular use of lipstick containing gritty materials might scratch the lips over time2. Undispersed pigments have a maximum particle size of 40 µm [11]. **Procedure:** A little amount of lipstick paste can be applied by pressing and spreading it on a glass slide with the help of another glass slide. After then, the glass slides are detached. One of the slides was observed using a microscope and a carefully calibrated eyepiece. It is now possible to determine the size of the biggest pigment particle [10].

2.3.5 pH measurement

The pH of the skin has an impact on a number of factors, such barrier homeostasis, cohesiveness, as well as the mechanisms of bacterial defense. Rising desquamation, dry and scaly skin, as well as an ideal habitat for the growth of pathogenic bacteria, result from an increase in pH. Maintaining the acidic pH of the skin is so critical. The pH of the skins surface is usually slightly acidic, ranging from 5 to 9.5, based on gender and body site [2]. **Procedure**: In a 200 mL beaker, weigh 5 g of lipstick. Heat the mix to 45 degrees Celsius and stir for many mins after adding 90 mL distilled alcohol. Pour the mixture over filter paper to separate the alcohol, then eliminate the leachate & measure its pH at 27 ° C [12].

2.3.6 The determination of heavy metal

Some elements and compounds in cosmetics have been banned or severely restricted under Saudi Specification SASO 2825/2011, like antimony and its compounds, arsenic, some barium salts, the element bromine, cadmium and its compounds, chromium, gold salts, phosphorus compounds, potassium cyanide, inorganic iodine, lead and, its compounds (excluding lead acetate), mercury, certain thallium compounds, zirconium compounds, strontium, and selenium. Arsenic, cadmium, cobalt, chromium, mercury, nickel, and lead are among the heavy metals under study. In addition, Ti and Zn in the samples were evaluated as TiO2 % and ZnO %, respectively. As per SASO 2185/2003 and Health Canada, cosmetics can include up to 25% TiO2 and ZnO Table 1.

2.3.7 Procedure

Wet digestion of samples with concentrated HNO_3 (concentration 69.99%) was done followed classic preparation methods [16].

2.3.8 ICP-OES conditions

The elemental content of lipstick samples has been analyzed using a Perkin Elmer Optima 8300 (USA). The following are the device requirements: Plas: 10 L/min; Aux: 0.2 L/min; Neb: 0.70 L/min, Power wat: 1350; View dist.: 15.0; Plasma view: Axial.

3. RESULTS AND DISCUSSION

Results of all experiments will show consecutively, and then extract the summation that indicates the safety or hazard of lipstick samples.

3.1 SASO Experiments Results

Visual inspection outcomes: The samples under examination were visually inspected as per the SASO1871/200911 specification, and all samples were found to be acceptable.

3.1.1 Peroxide number (rancidity) results

The peroxide number obtained from the low-cost samples (1, 2, 3, and 4) is higher than the allowable limit of the SASO 1871/2009 [11] standard (> 10) and so they are banned. Whereas, samples no. (5, 6, 7, 8, 9, 10, 11, and 12) which ranged values (from 5.16±0.26 to 9.61±0.15) are approving. Rancidity calculated by equation $=\frac{\mathbf{A\times N\times 100}}{\mathbf{mass\ of\ Sample}}$, where A= volume in mL of sodiumthiosulphate, N= normality of sodiumthiosulphate solution. No. of determination: 3

3.1.2 Microbiological examination findings

All samples passed the microbiological examination within SASO 1871/2009 [11] approved limits; the maximum value permitted in lipstick has to be 100 CFU/ml. The sample with the highest bacterial count is sample no. 9, which has 41.00 ±1.03 CFU/ml. No. of determination: 3

3.1.3 Softening point findings

This test is used to determine lipsticks stability at high temperatures. Lipsticks minimum melting point ought to be 55 ° C, as per SASO 1871/2009. When carrying out such test upon lipstick samples, five low quality and shipper sample no. (1, 2, 3, 4, and 5) were melting under 55 °C, so they are banned, implying that they shouldnt be sold in Saudi Arabia. Another medium to expensive brand samples no (6, 7, 8, 9, 10, 11, and 12) were approving SASO specification, their softening point ranged (from 55.33 ±2.03 to 58.5 ±1.52). No. of determination: 3

3.1.4 The Particle size of undispersed pigments produces

Smaller particles (in the range of 20 µm) produce silky and satin impacts, in addition to pacifying the mass. Larger-sized particles (in the 120 µm range) produce high luster, glittering, sparkling, great brightness, and transparency impact) [2]. The permitted limit, as per SASO 1871/2009, is particles with a diameter of up to 40 µm. The particle size of undispersed pigments in all lipstick samples ranged between 15.04 ± 0.15 µm and 34.67 ± 0.31 µm, showing good results. No. of determinations: 3

3.1.5 Results of pH measurements

Lipstick acidity must be controlled for healthy lips, since excessive pH may induce cracks, corrosion and damage. As per the SASO 1513/201012 cosmetics specification, permissible pH values varied from 5 to 9.5. The specification criteria were fulfilled by all of the samples under examination. Results of pH ranged between 6.29 ±0.21 and 7.92 ±0.37 values. No. of determinations: 3

3.2 Heavy Metals Determination

3.2.1 Linearity, recovery, LOD, and LOQ

The linearity of an analytical process is defined as the ability of an analytical process to produce test findings which are processed directly or via well-organized mathematical changes, and are equivalent to the concentrations of analytical samples within a specific limit [17]. Three replicates of the blank matrix have been spiked with heavy metal standards to assess extraction recovery. The lipstick sample has been split into 2 groups: A1 was spiked with 0.25 ppm standard prior to digestion, and A2 was spiked with 0.25 ppm standard following digestion however before ICP-OES injection. Using Eq. Recovery (%)= (A1-Blank)/(A2-Blank) × 100, the percentage of extraction recovery has been estimated by comparing the concentration of heavy metals prior microwave digestion to the concentration spiking following digestion in the blank matrix [18].

For any analytical process, a statistical method based on measuring duplicate (negative) samples, or an experimental method, has been used to determine the limit of detection (LOD=(3×SD)/Slope) and limit of quantification (LOQ= (10×SD)/Slope), i.e. the concentration at which quantitative data are being revealed with a high level of confidence [19].

The linearity, recovery, LOD, and LOQ ranges in Table 2 show that the approach has good accuracy. The average extraction recovery ranges between 85.99 and 117.84%. With coefficients of determination (R2) ranging from 0.9992 to 0.9999, the calibration curve exhibits good linearity.

Table 1. Heavy metals, TiO2, and ZnO regulatory limits in lipsticks

Elements	SASO A	FDA B	Health Canada C
As	2.5 ppm	-	< 3 ppm
Cd	1 ppm	-	0.5 ppm
Co	-	15 ppm	-
Cr	-	5 ppm	-
Hg	0.5 ppm	< 1 ppm	< 1 ppm
Ni	-	< 200ppm	-
Pb	10 ppm	20 ppm	10 ppm
TiO2	25%	-	25%
ZnO	-	-	25%

A [13]; B [14]; C[15]

Table 2. Linearity, recovery, LOD, and LOQ

Element	R2	Range(mg/l)	Recovery	LOD (mg kg-1)	LOQ (mg kg-1)
As	0.9992	0.5-100	99.94%	0.545	1.995
Co	0.9994	0.5-100	100%	0.027	0.089
Cr	0.9995	0.5-100	100%	0.031	0.103
Cd	0.9994	0.5-100	85.99%	0.061	0.381
Hg	0.9802	0.0-60	100%	0.090	0.302
Ni	0.9995	0.5-100	100%	0.012	0.041
Pb	0.9999	0.5-100	117.48%	0.129	0.431
Ti	0.9997	0.5-100	100.36%	0.186	0.621
Zn	0.9993	0.5-100	100.66%	0.047	0.157

LOD: limit of detection, LOQ: limit of quantification, R2: correlation of determination

Table 3. Assessment of intra-day and inter-day precision:

Metal	Lipsticks content Average ± SD (n=3)		% (RSD)	
	Intra-day	Inter-days	Intra - day	Inter- days
As	1.65±0.02	1.63±0.06	1.21%	3.68%
Cd	ND	ND	ND	ND
Co	0.30±0.01	0.28±0.01	3.33%	3.57%
Cr	5.41±0.01	5.44±0.12	10.51%	10.57%
Hg	ND	ND	ND	ND
Ni	0.15±0.01	0.15±0.02	6.67%	13.33%
Pb	1.90±0.02	1.92±0.05	1.05%	2.60%

3.2.2 Method validation information

Precision: Samples were analyzed on 2 separate days, a week apart, to see how accurate the ICP-OES was and how stable the samples had been. The element concentrations on various days were very close, as seen in Table 3. The ICP-OES has been a very accurate and convenient technique for such type of analysis, and such findings demonstrate that the samples were stable.

3.2.3 Duplicate samples precision and agreement

Table 4 displays the individual findings for two lipstick 3 sample digestions, as well as the standard deviation (SD) and relative percent difference $\mathrm{RPD} = \frac{(V1-V2)}{(V1+V2)/2} \times 100, \mathrm{v1: concentration1, v2: concentratio}$) between the two-measured concentrations. The RPD is less than 5%, which shows good agreement between the duplicate digestions.

3.2.4 Elemental analysis findings

Table 5 show heavy metal concentrations (As, Co, Cr, Cd, Hg, Ni, and Pb) in mg/kg units (i.e. ppm) in lipstick samples, as well as titanium and zinc concentrations in mg/kg units (ppm). The calculation equation is as follows:

$$\text{Element} = \frac{\text{conc. Of element in samples } (\mu g/L) \times \text{mL of sample}}{\text{Sample weight (g)} \times 1000} \ \mu g/g$$

For 12 lipsticks products, all heavy metals investigated were identified. Each metals concentration differed between lipsticks. The highest concentration was zinc, which had an average value of 564 ppm, whereas the lowest was chromium, which had an average value of 0.1 ppm. The average metallic concentrations in the 12 lipsticks were as follows: Zn > Cd > Pb > Cr > As > Ti > Ni >Co > Hg. All of the samples were free of mercury.

Table 5 shows: All samples contained lead, with the exception of samples 8-12, that are more expensive and of higher quality. Lead concentrations varied from 1.90 to 125.30 ppm. The cheapest samples 1 and 2 had the highest concentration; light color sample 2 had a greater concentration than dark color sample 1. Pb was discovered in all samples with amounts up to 123 ppm, according to Table 5, however our research found quantities up to 125.30 ppm. As per SASO, lead levels have to be less than 10 ppm, or less than 20 ppm, as determined by the FDA. Four samples (1, 2, 4, & 7) do not match the SASO criteria, according to the findings. Low lead levels in ladies of childbearing age could have a negative impact on their reproductive health and/or the health of their children. Excessive lead exposure alters nerve conduction and inhibits the availability of calcium in the body [20].

Cadmium was found in only 3 samples, nos. 1, 2, and 6, at amounts of 418.50 ppm, 158.85 ppm, and 15.3 ppm, respectively. The largest concentration was found in samples 1 and 2, which were less expensive. The concentration is higher in the dark color sample no. 1 than in the light color sample no. 2. Cd was identified in numerous studies, with values up to 141.04 ppm, as per Table 5; however, the concentration in this research was 418.50 ppm. For SASO, Cd levels should not exceed 1 ppm, and for Health Canada, they should not exceed 0.50 ppm. Three of the samples, nos. 1, 2, and 6, exceed the SASO and Health Canada standards. Nausea, vomiting, diarrhea, convulsions, shock, as well as kidney failure are all symptoms of acute Cadmium exposure [21].

Eight samples were found to contain Cr, with amounts varying from 0.10 ppm to 66.95 ppm. The highest concentration is found in sample no. 4, which is less expensive and has a dark color, whereas the lowest concentration is found in sample no. 9, which is more expensive and has a light color. When those outcomes are compared to the values in Table (6), we can observe that our study had a high chromium concentration, rising as high as 40.80 ppm. A small amount of chromium is required for good health; however excessive amounts may lead to hepatic, stomach, and renal problems, as well as irritation, runny nose, bloody nose, and possibly death [3].

Arsenic was identified in all samples, with average amounts ranging from 1.40 to 59.95 ppm. The largest concentrations were found in the less expensive samples 1 and 2; the concentration in light colour one sample 2 is more than in dark color one sample 1. Arsenic was found in earlier studies up to 6.52 ppm, while it was found up to 59.95 ppm in this research, as per Table 5. As per SASO, arsenic concentrations have to be less than 2.5 ppm, while the FDA requires less than 3 ppm. Only two samples, nos. 3 & 8, were beneath the SASO and FDA acceptable limit, whereas ten samples failed to meet the SASO criteria. Arsenic exposure may have devastating consequences. Symptoms of extreme overexposure include a wide range of symptoms, from nail striation to skin infections and even alopecia [22].

All samples contained cobalt, with concentrations ranging from 0.20 to 4.50 ppm, with the exception of sample 1. The lowest concentration is in sample no. 1, whereas the highest concentration is in sample no. 4. The sample with the highest cobalt concentration is the cheapest. The concentration is higher in the light color sample no. 4 than in the dark color sample no.3. Table 5 shows that cobalt was found in Pakistani and American research with quantities up to 5.30 ppm, which is close to the 4.50 ppm found in our research. As per the FDA, the cobalt limit is 15 ppm, hence all of the samples were safe to consume. Cobalt is required in small levels for human health, if only because it is the active component of vit B12. In allergic people, cobalt was proven to induce or exacerbate dermatitis [20].

No mercury was discovered in any of the samples examined. The SASO sets a 0.50 ppm mercury limit for cosmetics, while the FDA sets a 1 ppm limit. Signs of mercury poisoning include insomnia, tremor, memory loss, neuromuscular impacts, headaches, thinking problems, and motor dysfunction [20].

Ni was found in all samples at concentrations ranging from 0.15 to 6.25 ppm. Ni concentration was greatest in sample no. 4, which had a bright pink color, and lowest in sample no. 3, which had a dark color. According to Table 5, nickel was identified in amounts as high as 13.00 ppm, but our research found up to 6.25 ppm, indicating the evolution of cosmetic product quality. When nickel comes into touch with the skin, it creates a type of irritation known as allergic contact dermatitis. Nickel is also carcinogenic and teratogenic. Nickel is found in significant concentrations in DNA and RNA, as well as lipids, hormones, and cell membranes [20].

Sample no. 1 had the greatest overall heavy metal concentration in the examined lipstick products, having an overall concentration of 579.90 ppm. This sample is a low-quality, low-cost lipstick with a dark color. Sample no. 2 had the 2nd greatest metal concentration, with 346 ppm of metals found; this sample was a high price brand and had a dark color.

Since no lead was found in samples 8, 9, 10, 11, and 12, they were considerably safer, as lead is normally present in lipstick in low concentrations.

3.2.5 Calculation of titanium dioxide and zinc oxide percentages

Table 7 shows the percentages of TiO_2 and ZnO compounds in lipstick samples. The following equation was used to calculate the percentage of TiO_2 in the samples: $TiO_2\% = Ti\ result \times (Mwt.TiO_2 / At\ wt\ Ti) \times 10^{-7}$, Mwt TiO_2 / At wt Ti = 1.6685, We used the following equation to calculate the percentage of zno: $ZnO\% = Zn\ result \times (Mwt.\ ZnO / At\ wt\ Zn) \times 10^{-7}$, Mwt ZnO / At wt Zn = 1.24

With the exception of sample no. 6, titanium was discovered in all samples, with concentrations varying from zero 36.00 ppm. The greatest concentration of Ti was detected in sample no.4 (36.00 ppm) that is a low-cost light-colored sample; the deep-colored sample (sample no. 3) of the same brand had a value of 2.3 ppm. Ti was found in lipstick in amounts varying from 4.46 to 1418.00 ppm, as shown in Tables 6. Sample no. 4 had a larger concentration of TiO_2 ($6\times10^{-3}\%$), whereas sample no. 2 had the lowest proportion ($1\times10^{-4}\%$). Such TiO_2 levels are within the SASO 2185/2003 standards limits that permit TiO_2 to be used as a preservative or colorant in cosmetic products up to a 25% concentration.

With the exception of sample no. 3, Zn was discovered in all of the samples, with measured concentrations varying from 6.80 to 564.00 ppm. Sample no.11 (measured at 564.00 ppm), an expensive sample with a deep color, had the greatest proportion of zinc. The concentration in the same brands light color sample, no. 12, was 43.85 ppm. Table 5 shows that Zn was found in all lipsticks in earlier studies, with rates varying from 88 to 101 ppm; in this research, the observed levels ranged up to 564.00 ppm. Zinc is not toxicologically significant, hence it is safe to use in lipstick, however zinc oxide can be dangerous. The FDA hasnt set a limit for zinc in cosmetics, while titanium oxide has a 25% allowable maximum. Zinc appears in cosmetics as zinc oxide, similar to titanium. Zinc oxide percentage concentrations ranged from 7.47×10^{-5} % to 0.16 %, indicating that this component was present at levels well under the acceptable limit in all of the lipsticks examined. Sample no. 11, that had a dark color, had the highest concentration of ZnO.

3.2.6 Relationship among all experiment outcomes

3.2.6.1 Table 8 compares the outcomes of all experiments

The microbiological investigation, particle size of undispersed colors, and pH measuring testing were all passed by sample nos. 1, 2, 3, and 4 (the less expensive samples). As per SASO, the melting points of such samples were lower than the allowed limits. Such samples had a peroxide number that was higher than SASOs allowed limit. Furthermore, the overall toxic element content of such samples was high, reaching 579.9 ppm, owing to the high lead concentration in samples 1 and 2. In addition, sample nos. 3 and 4 had elevated arsenic and chromium concentrations. As a result, these four samples were deemed unsafe for use.

All SASO tests for lipsticks have been passed by samples 5, 6, 7, and 8, with the exception of the melting point (samples with a middle price). Sample 5 had a melting point of 53.66 oC, that was slightly lower than SASOs permitted limit of 55 0C. Those samples have elemental concentrations of 62.65 ppm. In sample 6, the highest total metal concentration was owing to arsenic and cadmium.

All SASO lipstick tests were passed by samples 9, 10, 11, and 12 (expensively cost samples). The overall toxic element concentration in such samples was 22.05ppm, owing primarily to arsenic, which was found in all samples. Because such samples did not contain any lead, they are considered to be safer than other samples.

3.2.7 Correlation between the experimental findings and the questionnaire

According to the survey, 34.5 % of ladies noted that their lipsticks melted in hot weather; as an outcome of the experiments, there have been five samples (1, 2, 3, 4, and 5) with melting points at temps lower than the SASO acceptable limit. These lipstick samples were from less expensive brands, and it turns out that the majority of the ladies polled use less expensive lipstick. This is a sign of the poor quality of inexpensive lipsticks.

With pH findings varying from 6.29 to 7.92, all samples beneath examination passed the pH test below the SASO permitted limit (acceptable pH range 5-9.5). Bacterial growth and irritation of the lips are caused by an acidic pH. According to the surveys findings, 60.7 % of ladies did not perceive a difference in their lips. This means that the majority of lipsticks on the market are pH-safeHHH.

45.6% of ladies think bacteria can be found in lipstick, despite the fact that all of the samples bacterial counts are within SASOs allowed limits. This implies that, despite popular belief, the samples have been safe to use.

97% of the ladies polled use lipstick between 1 and 5 times per day, with 51 % opting for a less expensive brand. The findings of this research suggest that the lower-cost samples have a significant concentration of toxic components, raising concerns about the usage of such types of lipstick, which could harm ladies or fetuses. Several studies have found that toxic components can be detrimental at very low levels, according to the literature review Nnorom et al. [27].

Since oil and fats are key components of lipstick, rancidity can happen, particularly when improper storage conditions and subjected to elevated temperatures are considered. According to the findings, the sample with the lower price had a higher peroxide number than the SASO permitted limit. According to the survey, 35.9% of ladies noted a difference in the fragrance of lipsticks following prolonged use, which is most likely due to the high peroxide number.

Table 4. Duplicate samples precision and agreement (mg/g)

Elements	Lip3 A	Lip3 B	Average	SD	RPD
As	1.65	1.63	1.64	0.01	1.22%
Cd	ND	ND	-	-	-
Co	0.30	0.28	0.29	0.01	6.89%
Cr	5.41	5.44	5.43	0.02	0.55%
Hg	ND	ND	-	-	-
Ni	0.15	0.15	0.15	0.00	0.00
Pb	1.90	1.92	1.91	0.01	1.05%

Table 5. Analyses of toxic elements

Sample No.	ppm ± SD for element concentration							
	Limits of detection (ppm)							
	As	**Cd**	**Co**	**Cr**	**Hg**	**Ni**	**Pb**	
	0.05	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**	**Total**
1	53.95±0.05	418.5±1.04	ND	1.60±0.01	ND	1.35±0.01	104.15±0.55	579.9
2	59.95±0.11	158.85±0.31	0.20±0.01	ND	ND	1.70±0.01	125.3±0.23	346
3	1.65±0.82	ND	0.30±0.03	5.40±0.01	ND	0.15±0.01	1.90±0.02	9.4
4	26.95±0.25	ND	4.50±0.02	66.95±0.11	ND	6.25±0.15	7.90±0.02	112.55
5	35.15±0.14	ND	1.50±0.01	2.15±0.02	ND	2.75±0.03	20.35±0.01	61.9
6	11.5±0.22	15.3±0.18	0.90±0.08	ND	ND	1.00±0.01	1.01±0.01	29.7
7	20.35±0.18	ND	1.55±0.14	13.75±0.01	ND	3.00±0.01	24.00±0.05	62.65
8	1.40±0.13	ND	0.50±0.03	ND	ND	1.62±0.01	ND	3.5
9	10.6±0.17	ND	2.30±0.16	0.11±0.01	ND	3.95±0.17	ND	16.95
10	7.45±0.11	ND	0.30±0.01	ND	ND	1.35±0.01	ND	9.1
11	18.50±0.16	ND	1.00±0.01	0.45±0.01	ND	2.10±0.01	ND	22.05
12	8.95±0.11	ND	0.55±0.01	0.3±0.01	ND	1.00±0.01	ND	10.8

Table 6. Heavy metal levels in lipstick cosmetics in the literature for various countries

Country	Cosmetics	Elements detection	Technique	As ppm	Cd ppm	Co ppm	Cr ppm	Hg ppm	Ni ppm	Pb ppm	Ti ppm	Zn ppm	References
Saudi Arabia	Lipsticks	Pb, Cr, Cd	Laser-induced breakdown spectroscopy (LIBS)	-	4.90 - 10.60	-	9.30 - 40.80	-	-	5.70 - 8.10	-	7.70 - 14.70	[21]
Saudi Arabia	Lipsticks	Pb, Cd, Ni, Cr Hg, As	Atomic absorption spectrophotometer (AAS)	0.17 - 6.52	0.00 - 0.08	-	0.17 - 16.54	0.00 - 0.01	0.12 - 4.24	0.30 - 2.44	-	-	[20]
Iran	Lipsticks	Pb, Cd	Flame Emission Spectrophotometer (FES)	-	0.60 - 1.10	-	-	-	-	7.00 - 40.00	-	-	[23]
Turkey	Lipsticks	Pb	Electrothermal atomic absorption spectrometry (ET-AAS)	-	-	-	-	-	-	0.11 - 4.48	-	-	[24]
Pakistan	Lipsticks	Pb, Cd, Cr, Ni	(AAS)	-	0.20 - 0.50	0.22 - 5.43	-	-	0.06 - 5.94	0.28 - 6.23	-	-	[3]
United States of America	Lip products	Pb, Cd, Co, Cr, Cu, Ni, Ti.	(ICP-OES)	-	0.00 - 3.48	0.01 - 1.30	0.01 - 6.05	-	0.01 - 9.73	0.02 - 1.25	4.64 - 1418.00	-	[25]
Malaysia	Lipsticks	Pb, Cd, Cr	(ICP-OES)	-	0.06 – 0.33	-	0.48 – 2.50	-	-	0.77 - 15.44	-	-	[18]
Saudi Arabia	Lipsticks	Pb, Cd, Hg, As	Graphite furnace-atomic Absorption Spectrometry. (GFAAS)	0.00 - 0.15	0.00 - 0.002	-	-	0.03 - 1.52	-	0.00 - 0.04	-	-	[9]
China	Lipstick	As, Cd, Cr, Ni, Pb	(ICP-MS)	0.00 - 0.14	0.00 - 0.01	-	0.00 - 1.67	-	0.00 - 4.35	0.00 - 0.13	-	-	[26]
This Study	Lipsticks	As, Co, Cr, Cd, Hg, Ni, Pb, Ti, Zn	(ICP-OES)	1.65 - 95.59	15.30 -418.50	0.20 - 4.50	0.10 -66.95	ND	0.15 - 6.25	1.00 -125.30	0.02 - 36.00	6.80 - 564.00	This study

Table 7. Percentages of titanium dioxide and zinc oxide

Sample	Ti concentration ppm±SD	TiO2%	Zn concentration ppm±SD	ZnO %
1	0.21±0.01	3.34×10-3	119.45±0.60	0.01
2	0.62±0.02	1×10-4	60.00±0.31	7.47×10-5
3	2.30±0.01	3.83×10-4	ND	ND
4	36.00±0.15	6 ×10-3	468.05±0.42	0.07
5	17.15±0.01	2.86 ×10-3	37.00±0.07	4.60×10-3
6	ND	ND	102.15±0.14	1.36×10-3
7	24.2±0.01	4.04 ×10-3	130.85±0.01	0.02
8	5.65±0.01	9.42 ×10-4	6.8±0.02	8.46×10-6
9	4.82±0.01	8.01 ×10-4	32.85±0.17	4.17×10-3
10	7.35±0.01	1.23×10-3	58.7±0.02	7.31×10-3
11	15.4±0.03	2.57×10-3	564.00±0.17	0.16
12	20.85±0.01	3.48×10-3	43.85±0.01	5.45×10-3

ND : Not detect

Table 8. Results of all experiments

Samples Experiments	1	2	3	4	5	6	7	8	9	10	11	12	Specification Limit
Microbiological examinations CFU/ml	21.66	1.66	29.33	15.00	3.66	19.66	22.00	19.66	41.00	30.00	9.66	28.33	100
Peroxide number	13.48	13.69	12.96	12.79	9.61	9.42	9.00	7.97	6.04	6.90	5.16	5.95	10
Softening point 0C	49.66	50.50	50.13	49.43	53.66	55.33	56.00	58.5	57.33	57.00	56.66	55.66	≥55
The Particle size of undispersed pigments (µm)	34.30	16.57	21.28	17.89	19.94	15.04	16.37	25.64	21.66	25.53	32.43	34.67	40
pH measurement	6.29	6.65	7.33	6.96	7.92	7.80	7.62	6.68	7.83	7.31	7.52	6.89	5.0-9
ICP results (ppm)	579.90	346.00	9.40	112.55	61.92	29.74	62.65	3.50	16.95	9.12	22.05	10.81	-
TiO2 %	3.34 ×10-3	1.00 ×10-4	3.83 ×10-4	6.00 ×10-3	2.86 ×10-3	ND	4.04 ×10-3	9.42 ×104	8.01 ×10-4	1.23 ×103	2.57 ×10-3	3.48 ×10-3	25%
ZnO %	0.01	7.74× 10-5	ND	0.07	4.60 ×10-3	1.36 ×10-3	0.02	8.46 ×106	4.17 ×10-3	7.31 ×103	0.16	5.45 ×10-3	25%

4. CONCLUSIONS

The concentrations of arsenic, cadmium, cobalt, chromium, mercury, nickel, and lead in numerous lipsticks from various brands were determined in this research. A digestion approach that uses an ICP-OES produces a clear outcome that is easy, rapid, and excellent; the procedure produced very precise findings and may be used for routine tests.

According to the findings, cheaper lipstick samples had toxic heavy metal concentration over the permitted limits that could be harmful to human health. Most of the less expensive samples under examination failed the basic peroxide number and melting point tests.
In terms of heavy metal concentration, high-end lipstick brands are not always safe. Heavy metal concentrations are often higher in dark-colored samples than in light-colored samples, this indicates the effect of heavy metals concentration which gives the degree of color for lipsticks. Under the allowed limits, TiO_2 and ZnO were discovered on all samples.

For items designed to come into indirect and long-term contact with skin, regulatory authorities must perform extensive quality controls and screening, especially for products imported from various nations. Consumers must stay informed and aware of the ingredients in the products they consume.

CONSENT

It is not applicable

ETHICAL APPROVAL

It is not applicable.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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