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Investigation of Potentially Toxic Elements (PTEs) Concentrations in Natural and Synthetic Product Cosmetics Used in Lagos, Nigeria

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Abstract:- The use of cosmetics in their various forms has been historical and still trending. Potentially toxic elements (PTEs) have been found to be critical constituents of these cosmetics, though as either functional ingredients or as impurities. This has raised health concerns such as; in kidney failures, heart diseases and birth defects. This study investigate the presence and levels of certain indexed PTEs in both natural and synthetic cosmetics and their associated health implications on users in Lagos State, Nigeria. Three natural product cosmetics namely; palm kernel oil (PKO), shear butter and 'tiro' labelled as NC1, NC2 and NC3 respectively, and five brands of synthetic product cosmetics (SPCs) labelled as SC1, SC2, SC3, SC4 and SC5 were selected for analysis based on questionnaire response to cosmetic use among Badagry women. The metal analysis done using ICPOES showed that NC3 is PTEs laden; Mn (38.132 ± 8.195) ppm, Ni (42.04 ± 2.331) ppm, Pb (65.341 ± 3.064) and Zn (92.89 ± 6.62) ppm. Mn concentration is the highest amongst all the SPCs, ranging from 17.56 ± 2.09 ppm to 29.04 ± 0.012 ppm. Ni concentration ranged from 0.506 ± 0.073 ppm to 9.88 ± 1.43 ppm. The presence of these PTEs could be attributed to unintended contamination from raw material or product processing, or deliberately added as part of the required ingredients as in the case of some synthetic cosmetics. The level of PTEs in the synthetic cosmetics were below the permissible limits set by WHO. However, the risk of bioaccumulation exists due to continuous use over time.

Keywords:- *Cosmetics, ICPOES, Kohl, Metal bio-intake, PTEs, Toxicity.*

I. INTRODUCTION

Cosmetics could be referred to as substances that are being applied on to (or introduced into) the human body by rubbing on, pouring, sprinkling, spraying or other means; with the intention of cleansing, enhancing beauty, promoting attractiveness, or modifying one's appearance[1,2]. Cosmetics are extensively utilized for regular body care which include; the skin, hair, nails, and teeth[3]. There are a wide range of cosmetic products including; creams, emulsions, lotions, gels, oils, face masks, tinted bases, make up powders, toilet soaps, perfumes, shower and bath preparations, deodorants and antiperspirants, depilatories, hair care and shaving products[3,4,5]. According to the production ingredients, cosmetics can either be herbal (materials of natural origin and are of gentler and less complex chemical based) or synthetic (those which are conventional and of complex chemical based)[6]. Among the most used skin cosmetics are those made of ingredients such as formaldehyde and formaldehyde releasing ingredients, hydroquinone, parabens, and phthalates which could be harmful to human body[7]. Cosmetics products have also been discovered to contain certain potentially toxic elements (PTEs)[4,7,8]. Among these products, skin care items such as lightening creams (also known as toning creams) and moisturizers are highly implicated[9]. PTEs are elements that can be harmful to human health at certain concentration levels. These elements can occur naturally in the environment, but they can also be introduced by human activities like mining, agriculture and industrial explorations. Examples of PTEs include lead, mercury, arsenic, cadmium, nickel, chromium, manganese, antimony and copper[7,10]. The toxicity of PTEs is accomplished by their ability to bind to one or more reactive groups in the human body which is essential for normal physiological functions. These metals bind to the enzymes and prevent them (enzymes) from working properly, stopping, or altering their metabolic process[11]. Mercury, out of all the PTEs, is known to be toxic in its elemental form while the others are more dangerous in their cationic forms; for example, Pb^{2+} or Pb^{4+}; Cd^{2+} and As^{3+}. The cations have a strong affinity for SH (in sulfhydryl, thiol or mercaptan) groups which are found in proteins (muscles in the body) and enzymes[11,12,13].

PTEs have been found to cause adverse effects when present in higher concentrations. Cancerous breast biopsies demonstrate higher accumulations of nickel, chromium, cadmium, mercury, and lead compared to non-cancerous biopsies, and some metals can mimic estrogen in the presence of certain breast cancer cells[14]. Lead, which may be present as an impurity cosmetics, is a well-established neurotoxin linked to learning and behavioral issues[11]. Furthermore, exposure to lead has been linked to miscarriage and reduced fertility in both

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males and females, hormonal fluctuations, irregular menstrual cycles, and delayed puberty onset in girls[15]. During puberty, boys with developing testes may be especially susceptible to lead bioaccumulation. Pregnant women and young children are also vulnerable as lead can cross the placenta and potentially enter the fetal brain[14,16,17,]. Mercury is associated with toxicity in the nervous system, as well as reproductive, immune, and respiratory systems. Thiomersal, a mercury-based preservative, which also contains mercury. Mercury poses significant risks during fetal development and can be easily absorbed through the skin[15]. Although mercury and thiomersal are not widely used as direct ingredients or impurities, their high toxicity raises concerns about their presence in any cosmetic product. Other PTEs exhibit a comparable toxic nature[13,14].

Acceptable limits for PTEs vary according to the sub-population of interest: for example, children are more susceptible to heavy metal toxicity than adults due to their high intestinal absorption capabilities, low effective excretion, and high food intake/body weight ratio[16]. Assessment of dermal absorption by a single component in a cosmetic product is complex and depends on factors such as the concentration in the product, the amount of product applied, the length of time left on the skin and the presence of emollients and penetration enhancers in the cosmetic product[5]. Given this complexity and the lack of well-conducted dermal absorption studies incorporating these factors, determination of PTE limits in cosmetics based on human health risk alone is a challenge[18].

To safeguard against excessive exposure to heavy metal ions, international regulations have been implemented to set limits on metal impurities in cosmetics[19]. A significant concern in the use of cosmetic products lies in their elevated levels of PTEs contents, primarily resulting from the industrial manufacturing processes.

II. MATERIALS AND METHODS

- *Research Design*

The experimental design involved the sampling of the natural cosmetics including *Ori*, Kernel oil and *tiro* (labelled as NC1, NC2 and NC3 respectively) and synthetic cosmetic creams namely B.B Clear, Visita Plus, Vaseline Even Tone, St. Ive Softening Lotion and Extract Toning Lotion (labelled as SC1, SC2, SC3, SC4 and SC5 respectively) from selected cosmetic stores and open markets in Badagry, Lagos. It also includes the laboratory analysis of the target PTEs in the samples which includes lead, mercury, cadmium, nickel, zinc, chromium and manganese using ICP-OES techniques. Data obtained were then analysed.

- *Sampling Technique*

Structured random sampling technique was employed to obtain branded SPCs and unbranded natural cosmetic products from selected markets in Badagry Lagos based on frequency of use as informed from the questionnaires administered. Three hundred and sixty-three (363) questionnaires were retrievable out of four hundred (400) administered among women within the age range of 18 to 36 years. Twenty-five major residential and business locations within Badagry Local Government of Lagos was considered in the questionnaire sampling. Four samples of each cosmetic products (both synthetic and natural) were collected for elemental spectroscopic analysis using ICPOES.

- *Sample Pre-treatment and Analysis*

About 5 ml of HNO_3 will be added to 1 g of each sample of the prepared brand hair dyes. After heating for 4 hours at 85 °C the sample will be cooled to room temperature and 1ml of hydrogen peroxide 30 % will be added and it will be injected to Inductively Couple Plasma-Optical Emission Spectrometry (ICP-OES) in order to determine the concentration of Cd, Cr, Hg, Mn, Ni, Pb, and Zn[20].

- *Digestion of Samples*

A 0.5 g sample of the cosmetic product was accurately weighed by using a four-decimal-place analytical balance and transferred to a screw-cap polytetrafluoroethylene digestion vessel. A mixture of 2.0 mL HNO_3 and 1 mL of 30 % H_2O_2 was added at room temperature and left to pre-digest for 12 h. The vessels were sealed and placed in the oven at 160 °C for 4 h. The vessels were allowed to cool to room temperature after the digestion process was complete. The digests were diluted to 10 mL with Milli-Q water and ready for ICP-OES analysis. For the analysis of Cd, Hg, Pb, and Ni, 1.0 mL of the diluted solution was added to a 5 mL vessel, and then 1 mL 5 % thiocarbamide and 3.0 mL 10 % nitric acid were added and left to react for 5 h at room temperature before ICP-OES analysis[20,21,22].

- *The PTEs Analysis using ICP-OES*

Analysis of the metals (Cd, Cr, Hg, Mn, Ni, Pb, and Zn) was done using the Agilent 5800 ICP-OES equipment. Standards concentrations for the heavy metals were used for the internal calibration equipment for the analysis. Instrumentation Parameter Rate 1450W, Plasma Gas Flow Rate at 15 L per min, Auxiliary Gas Flow Rate of 0.2 L per min, and Equilibration Time Rate of 15 sec with a read delay of 45 sec, and Ar gas as at heavy metal's specific wavelength.

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III. RESULTS AND DISCUSSION

Table 1: Description of the Products Analysed

ID	Product	Origin	Date of Purchase	Information as provided on the products
NC1	Palm Kernel Oil	Locally made in Okitipupa, southwestern Nigeria	Oct. 10, 2023	Edible oil, free from lead and other toxic metals
NC2	Shea Butter	Locally made in Okitipupa, southwestern Nigeria	Oct. 10, 2023	Local body cream, processed from the nuts of Shea trees, which is native to west Africa.
NC3	Tiro	Locally prepared in Saki, southwestern Nigeria	Oct. 10, 2023	Traditional eyeliner cosmetics found in southwestern Nigeria consisting majorly PbS and other elements (chalcogens)
SC1	B.B Clear	Skin toning cream from Togo	Oct. 15, 2023	Lightening the skin. Contains alpha hydroxyl acids (AHA)
SC2	Visita Plus	It is a skincare products manufactured in India	Oct. 15, 2023	Clotrimazole is a broad spectrum of antifungal agent that is used for treatment of dermal infections
SC3	Vaseline Even Tone	Product of USA, marketed worldwide	Oct. 21, 2023	For radiant lighter skin; contains vitamin B3, triple sunscreens
SC4	St. Ives Softening Lotion	Made in USA	Oct. 21, 2023	Lightens the skin naturally
SC5	Extract Toning Lotion	Product of UK	Oct. 21, 2023	Improves the skin's elasticity and delay aging

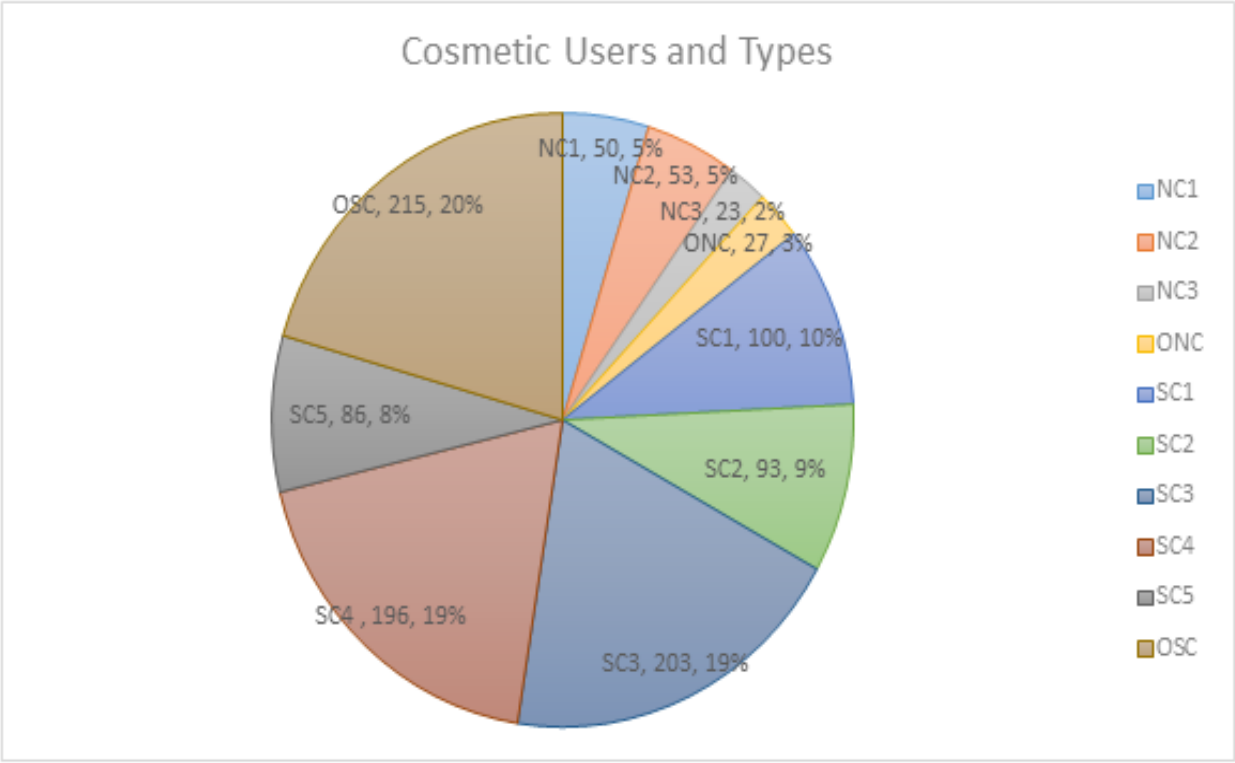

Fig 1: Questionnaire Synopsis for the 363 Cosmetics Users
ONC = Other Natural Cosmetic Products
OSC = Other SPCs

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Table 2: Concentrations (ppm) of PTEs in Selected Natural Cosmetic Products (for n = 4)

	Cd	Cr	Hg	Mn	Ni	Pb	Zn
NC1	0.018±0.003	0.005±0.037	0.012+0.04	1.546 ±0.099	0.634±0.084	1.413±0.602	1.869±0.031
NC2	0.054±0.024	0.189±0.039	0.053±0.05	0.540±0.012	0.506±0.073	2.651±0.943	1.781±0.014
NC2	2.045±0.034	0.232±0.058	0.062±0.041	38.132±8.195	42.04±2.331	65.341±3.064	92.89±6.62

Table 3: Concentrations (ppm) of PTEs in Selected SPCs (for n = 4)

	Cd	Cr	Hg	Mn	Ni	Pb	Zn
SC1	0.081±0.013	0.055±0.037	0.032+0.07	17.56 ±2.09	8.634±0.081	0.813±0.202	1.869±0.031
SC2	0.047±0.014	0.819±0.049	0.073±0.04	29.04±0.012	0.506±0.073	0.651±0.943	1.781±0.014
SC3	3.045±0.112	2.632±0.058	0.092±0.041	23.32±8.195	4.04±0.33	1.341±0.96	2.89±0.612
SC4	0.93±0.076	0.016±0.023	0.005±0.002	27.45±4.23	9.88±1.43	1.67±0.065	4.32±1.075
SC5	0.42±0.17	0.084±0.055	0.007±0.002	21.08±0.98	7.66±0.77	2.11±0.543	3.21±0.33

Table 1 depicts the selected cosmetic products and various dermatological claims the manufacturers made on the package sleeves, especially for the SPCs. All of the natural cosmetic products were compounded locally, in southwestern Nigeria, using simple physical methods of production. They were also being used by the indigenous south-westerners of the nation. Results from figure 1 show that majority (about 85 %) of the cosmetic users in badagry are using synthetic imported cosmetics. These range from various skin care to skin toning products and other synthetic cosmetics products that are having similar dermal-care functions as those considered and selected for analysis. Lagos Badagry is a cosmopolitan society, hence the high use of SPCs with various dermal-care claims. This could also be the reason for the low (15 %) use of natural cosmetic products in the city; categorically only 2 % of beauty 'makers' in badagry uses tiro, which is a locally mined face beauty cosmetic.

Metal (Mn = 38.13 ± 8.195, Ni = 42.04 ± 2.331, Pb = 65.241 ± 3.064 and Zn = 92.89 ± 6.62) ppm level of NC2 was expectedly high. This is due to the composition of the beauty substance that share very similarity with the Middle East and Asian 'Kohl' which is a natural facial cosmetic and mascara with major constituents of PbS; also being utilized just like NC2. Pb has been implicated in metal toxicity even in various other literatures[16,18,23]. Surprisingly, little amounts of Hg was found in all of the natural products investigated; NC1 = 0.012 ± 0.04 ppm, NC2 = 0.053 ± 0.05 ppm, and NC3 = 0.0062 ± 0.041 ppm. This is a major cause for concern due the potential toxicity of elemental mercury and its compounds. Hg can also bioasorb in the dermal tissue and later bioaccumulate in the entire system due to long term metal-exposure from cosmetic usage[24]. The levels obtained were however high when compared with Hg content of Kohl[25].

The SPCs were found to be low in metal contents, since major source of these products are petroleum and organic non-hydrocarbon based. Manganese was detected in both synthetic and natural cosmetics in significant quantities. The concentrations SC1 (17.56 ± 2.09) ppm, SC2 (29.04 ± 0.012) ppm, SC3 (23.32 ± 8.195) ppm, SC4 (27.45 ± 4.23) and SC5 (21.08 + 0.98) ppm were generally high in all the SPCS analysed. Manganese is an essential trace metal for biological systems, but excessive exposure to it can be toxic[26]. In humans, overexposure to manganese can lead to neurological deficits, characterized by mental difficulties and impaired motor skills. Manganese is generally not harmful to the skin, but its effects occur primarily when ingested through hand-to-mouth activities and sweating, thereby affecting the respiratory tract and the brain[27]. Manganese poisoning can result in hallucinations, forgetfulness, nerve damage, and bronchitis[28]. Long-term exposure may cause impotence in men, while chronic manganese poisoning can lead to permanent disability, with symptoms such as lethargy, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps, and paralysis[29]. The cosmetic product manufacturers should therefore source for a more friendly metal ingredients in the cosmetic formulations. Cosmetic users on their end should devise a mean to reduce exposure period to these synthetic products and guard against every means of metal ingestion, especially through the hand-to-mouth pathway[30,31].

IV. CONCLUSION

From the study, it can be concluded that SPCs are being used by majority of Badagry women. All of these cosmetics analysed were found to be high in manganese concentration, and this a serious concern to the users dermal and general health. Shea butter and Kernel Oil were found to be low in PTEs concentrations; the use should therefore be promoted among the local indigenes who prefers cosmetics made with natural ingredients. Tiro has been found to contain high Lead, Manganese and Zinc; the eyeliner should therefore be banned due to its metal toxicity tendencies. Every cosmetic user should also avoid hand-to-mouth ingestion of these products as that is the most medium of metal intake, even higher than dermal penetrations.

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