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Concentrations and exposure risks of some metals in facial cosmetics in Nigeria



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ABSTRACT

The concentrations of nine metals (Cd, Pb, Ni, Cr, Co, Cu, Fe, Mn and Zn) were determined in lip sticks, lip glosses, lip balms, eye pencils, eyeliners, eye shadows, blushes, mascaras and face powders. The study was aimed at providing information on the risk associated with human exposure to metals in these facial cosmetic products. The concentrations of metals in the samples were measured by atomic absorption spectrometry after digestion with a mixture of nitric acid, hydrochloric acid and hydrogen peroxide. The mean concentrations of metals in these facial cosmetics ranged from 3.1 to $8.4 \,\mu g \, g^{-1} \, Cd$, $12-240 \,\mu g \, g^{-1} \, Pb$, $9.1-44 \,\mu g \, g^{-1} \, Cr$, $18-288 \,\mu g \, g^{-1} \, Ni$, $1.6-80 \,\mu g \, g^{-1} \, Cu$, $7.9-17 \,\mu g \, g^{-1} \, Co$, $2.3-28 \, m g \, g^{-1} \, Fe$, $12-230 \,\mu g \, g^{-1} \, Mn$, and from $18 \, to \, 320 \,\mu g \, g^{-1} \, Zn$. The concentrations of Ni, Cr and Co were above the suggested safe limit of $1 \,\mu g \, g^{-1} \, for$ skin protection, while Cd and Pb were above the Canadian specified limits. The systemic exposure dosage (SED) values for these metals obtained from the use of these facial cosmetic products were below their respective provisional tolerable daily intake (PTDI)/or recommended daily intake (RDI) values. The margin of safety values obtained were greater than 100 which indicated that the concentrations of the metals investigated in these facial cosmetics do not present considerable risk to the users except in the case of face powders.

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1. Introduction

Cosmetics are used by all strata of society as a part of routine body care. In the past metals were used as ingredients of cosmetics, for example, the addition of the preservative thimerosal (mercury), lead acetate in progressive hair dye and red cinnabar (mercuric sulfide) in a number of tattoo pigments [1]. The deliberate use of metals as active ingredients in cosmetic products is prohibited by legislation in most countries, but metal impurities do exist in such products due to their persistence and ubiquitous natures. Metals such as Cd, Pb, Ni, Cr and Co are retained as impurities in the pigments of eye shadows or released by the metallic devices used during the manufacturing of these products. The continuous use of these cosmetic products could lead to the absorption

of metals through skin. Facial cosmetics are used daily and applied to the thinnest area of the facial skin, such as the peri-occular areas, and lips, where absorption may be very high [2]. Although, lipstick as a product is intended for topical use, it can be unconsciously ingested and therefore presents an obvious oral route of exposure to metal contaminants in cosmetics [3]. Metals are of environmental and human health significance because they exhibit a wide range of toxic and chronic health effects, such as cancer; reproductive, developmental and neurological disorders; cardiovascular, kidney and renal problems; lung damage; contact dermatitis; brittle hair and hair loss. Many are implicated as endocrine disruptors and respiratory toxins [4]. The use of cosmetics has been known to cause sensitization, dermatitis, allergic reactions and to be an important route of exposure to metals in humans as exemplified by the use of eye cosmetics such as kohl and surma.

Studies on the concentrations of metals in facial cosmetic products in Nigeria have been documented in the literature [1,5,6–8]. However, although most of the studies established the levels of metals in these facial cosmetic products, they paid little attention to systemic exposure dosages and risk evaluation of the elements

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investigated. The objectives of this study were to determine the concentrations and exposure risks of Cd, Pb, Ni, Cr, Cu, Co, Zn, Fe and Mn in some facial cosmetics in the Nigerian market.

2. Materials and methods

2.1. Sample collection

Samples of different brands of facial cosmetics (n = 160) were collected from cosmetics shops in Abraka, Warri, and Benin City in the southern part of Nigeria. The cosmetic samples were popular brands, some of which were produced locally and others imported. Most of the imported products examined were from the USA, China, Korea, India, France, Italy, Taiwan and the United Kingdom. The choice of brands was carefully made to reflect the types used by different income classes. The facial cosmetics were classified into eight broad groups, namely, (1) lipsticks, (2) lip glosses and balms, (3) eye shadows, (4) eye pencils, (5) eyeliners, (6) mascaras, (7) blushes and (8) face powders. The samples were stored under conditions similar to those of the retail shops until the analysis was completed.

2.2. Reagents

All reagents, nitric acid (HNO $_3$ 69% v/v), hydrochloric acid (HCl 37% v/v) and hydrogen peroxide (H $_2$ O $_2$ 30% v/v) were Suprapur® (Merck, Darmstadt, Germany). The calibration standards were prepared by diluting 1000 mg L $^{-1}$ commercial standards of Cd, Pb, Ni, Cr, Cu, Co, Zn, Fe and Mn (Merck, Darmstadt, Germany) with 0.25 mol L $^{-1}$ HNO $_3$.

2.3. Sample preparation

A mass of 1.0 g of each sample was placed into a Teflon vessel and treated with 20 mL of concentrated nitric acid, 10 mL of hydrochloric acid and 5 mL of hydrogen peroxide. The samples were covered and left to stand overnight. The following day, the samples were heated to 125 °C for 2 h. The clear supernatant solutions were allowed to cool, filtered and made up to 25 mL with 0.25 mol L^{-1} HNO3. Four blanks were prepared in a similar way, but omitting the samples.

2.4. Chemical analysis

All digested samples were analysed in triplicate for Cd, Pb, Ni, Cr, Cu, Co, Fe, Mn and Zn by means of flame atomic absorption spectrometry (PerkinElmer, Analyst 200, Norwalk CT, USA). Blank and calibration standard solutions were analysed in a similar way as the samples. In each batch of analyses, at least 3–4 blanks were analysed. The average blank signal was subtracted from the analytical signal of the sample before statistical analysis.

2.5. Quality control and statistical analysis

All glassware and sample vials were soaked in a solution of 10% nitric acid followed by thorough rising with distilled deionized water. The instrument was calibrated after every ten runs. In the absence of a certified reference material, a spike recovery method and an independent inter-laboratory comparison were used to validate the analytical procedure. The spike recoveries for the metals examined were Cd (97.6%), Pb (96.4%), Ni (93.2%), Cr (101%), Cu (92.4%), Co (98.2%), Fe (103%), Mn (96.7%) and Zn (97.2%). The relative standard deviations for replicate analyses ranged between 2.3–12.5% for all the elements quantified. The inter-laboratory study was carried out at the University of Ibadan, Multidisciplinary Central Laboratory, on 10% of the total samples. The results from

the inter-laboratory analysis showed strong agreement. The limits of detection and quantification (LODs and LOQs respectively) were evaluated on the basis of the noise obtained for the analysis of the blank samples (n = 3). The LOD and LOQ were defined as the concentration of analyte that produced a signal-to-noise ratio of 3 and 10 respectively. The limits of detection for the examined metals ($\mu g g^{-1}$) were Cd (0.23), Pb (0.1), Cr (0.6), Ni (0.8), Cu (0.08), Co (0.05), Fe (1.7), Mn (0.1) and Zn (0.8), and the limits of quantification ($\mu g g^{-1}$) were Cd (0.7), Pb (0.3), Cr (1.8), Ni (2.3), Cu (0.24), Co (0.15), Fe (5), Mn (0.3) and Zn (2.4). Analysis of variance and a Tukey multiple comparison test were used to determine whether the concentrations of metals varied significantly within the same group and between the different facial cosmetics respectively. All statistical analyses was carried by using SPSS software version 15.0 (SPSS Inc, Chicago, IL, USA).

2.6. Safety evaluation of facial cosmetic products

The risk of human exposure to metallic impurities in these facial cosmetic products can be assessed by making use of the uncertainty factor called the Margin of Safety (MoS). The MoS is the ratio of the lowest no observed adverse effect level (NOAEL) value of the cosmetic substance under study to its estimated systemic exposure dosage (SED) [9].

$$MoS = \frac{NOAEL}{SED} \tag{1}$$

The systemic availability of a cosmetic substance is estimated by taking into consideration the amount of the finished product applied to the skin per day, the concentration of metals in the cosmetic product under study, the dermal absorption of the metal and a human body weight value [9].

The systemic exposure dosage (SED) is given by the formula:

$$SED(\mu g \ kg^{-1} \ bw \ day^{-1}) = \frac{C_s \times AA \times SSA \times F \times RF \times BF}{BW} \times 10^{-3} \ (2)$$

where C_s is the concentration of metal in the facial cosmetic product (mg kg⁻¹) and AA is the amount of facial cosmetic product applied per day. The estimated daily amounts (ing) applied were 0.057, 0.51, 0.02, 0.005, 0.02 and 0.025 for lipstick/lip gloss/lip balm, face powder, eye shadow, eyeliner/eye pencil, blush and mascara respectively [9]. SSA is the skin surface area onto which the products are applied. The applied surface areas (in cm²) for the different facial cosmetic products were 4.8, 4.8, 563, 24, 3.2, 3.2, 24 and 1.6 for lipsticks, lip gloss/lip balm, face powder, eye shadow, eyeliner, eye pencil, blush and mascara respectively [9]. RF is the retention factor (1.0 for leave-on cosmetic products); F is the frequency of application per day; BF is the bioaccessibility factor; 10^{-3} is the unit conversion factor; and BW is the body weight (kg). A default body weight of 60 kg was used in this study. The values of AA, SSA, and RF used in this study were the standard values established by the Scientific Committee on Consumer Safety (SCCS) [9].

The NOAEL values were obtained from the oral reference doses (RFDs). The latter are "an estimate of the daily exposure to the human population (including sensitive sub-groups) that is likely to be without an appreciable risk of deleterious effects during life time" [9]. For the studied metals the NOAEL values were calculated by using the relationship, NOAEL = RFD × UF × MF, where UF and MF are the uncertainty factor (reflecting the overall confidence in the various data sets) and the modifying factor (based on the scientific judgment used) respectively. In this case the default values of UF and MF were 100 and 1. The RFDs (in mg kg $^{-1}$ day $^{-1}$) used were Pb (4 × 10 $^{-3}$)[10], Cd (1 × 10 $^{-3}$), Cr (3 × 10 $^{-3}$), Co (3 × 10 $^{-4}$), (Zn (3.0 × 10 $^{-1}$), Fe (7.0 × 10 $^{-1}$), Cu (4.0 × 10 $^{-2}$), Mn (1.4 × 10 $^{-1}$), and Ni (2 × 10 $^{-2}$)[11,12].

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