HEAVY METALS SPECIATION STUDY OF SOME SELECTED PERSONAL CARE PRODUCTS IN NIGERIA BY ATOMIC ABSORPTION SPECTROSCOPY

BY

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CERTIFICATION

This is to certify that this study was carried out by ASAFA Naheem Oladayo (SCP12/13/H/0040) under my supervision in partial fulfillment of the requirements for the award of Master of Science (M.Sc) degree in Chemistry, Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria.

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DEDICATION

This work is dedicated to Almighty Allah who has given me the opportunity to complete the work successfully and to my family.

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I give thanks and adoration to Almighty Allah for given me the golden opportunity to start and complete this programme in peace; I will always be a good servant to worship you.

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ABSTRACT

This study investigated the species of heavy metals such as As, Cr, and Pb in some customer care products available in Nigeria. This was done with a view to evaluating the associated health risks of these heavy metals with respect to the regular uses of the customer care products.

Common eleven classes of customer care products, namely; powder, toothpaste, nail removal, lip gloss, soap, liquid soap, body cream, hair relaxer, disinfectant, shampoo, and face cleanser, were selected and purchased from some supermarket stores in Ile-Ife, and analyzed for identification and quantification of heavy metals species. Approximately 250 mL phosphate buffer solutions (pH 2-8) were prepared by mixing appropriate amounts of sodium dihydrogenphosphate, disodium hydrogenphosphate, and phosphoric acid solution. Ten to thirty (10-30) mL of this buffer solution was added to 30 mL of a standard solution containing 20 ppm of each metal species of Cr, Pb, and As were stirred thoroughly until a required pH was attained using a calibrated pH meter. A glass column (12 cm in height, 1.2 cm in diameter) packed with 500 mg of Amberlite XAD16N resin was washed successively with methanol, water, 1 M HNO_3 in acetone, water, 1 M NaOH, and water sequentially to remove both organic and inorganic impurities and activate the resin. The column was preconditioned by passing phosphate buffer solution through it. A mixture of phosphate buffer and a solution of each metal species were passed through the column at a flow rate of 6 mL min^{-1}. After this, the column was rinsed twice with 10 mL of water. The

presented method was applied to the digested samples (powder , toothpaste, nail removal, lip gloss, soap, liquid soap, body cream, hair relaxer, disinfectant, shampoo, and face cleanser); the adsorbed metal species on the column was eluted with 10 mL of 1 M HCl in acetone. The eluate was analyzed for the determination of metal species concentrations of Cr, Pb and As using Atomic Absorption Spectrometry (AAS).

Total metal concentration of arsenic was observed to have the highest value among others in powder sample, Mp3 with 18.10 ± 0.30 ppm, followed by lead in powder (passion) with 4.80 ± 0.80 ppm, followed by chromium in soap (kasmo) with 4.70 ± 3.30 ppm. Speciation analysis indicated that lower oxidation species of these heavy metals with the exception of arsenic had lowest concentrations. With respect to speciation analysis, the highest concentrations of Pb(II) and Cr(III) were found in powder (Mp3) with 4.80 ± 0.80 ppm and soap (kasmo) with 4.63 ± 3.29 ppm, respectively, while the highest concentration of As(V) was observed in powder (Mp3) with 18.10 ± 0.30 ppm. The highest concentrations of Pb(IV) and Cr(VI) species were detected in tooth paste (Oral B) with 0.32 ± 0.01 ppm, and hair relaxer (Relax) with 0.15 ± 0.01 ppm, respectively, while the highest concentration of As(III) species was recorded in powder (Ballila) with 0.48 ± 0.01 ppm. Concentration of arsenic detected in most of the products were higher than the 3 ppm specified as the maximum permissible level in cosmetics, while lead levels were lower than the 10 ppm maximum acceptable levels in cosmetics.

This study concluded that personal care products investigated were contaminated by heavy metals species to levels that could constitute health hazards to the users

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

The term heavy metal chiefly arose with discussions of pollutants discharged to the environment, in the form of air, water or soil contaminants. Heavy metals are metallic element with density greater than 4.5 g/cm^3.

With the growing industrialization and urbanization from the last few decades, a large amount of heavy metals have been exposed to the environment leading to increased metal concentrations in air, water, soil and virtually every area of modern consumerism from construction materials to personal care products. Unlike organic pollutants, metals are not biodegradable and therefore can accumulate in the living organism easily.

Some trace metals are essential and play important roles in human metabolism. In some cases, they are intentionally added for one purpose or the other. For example, chromium is used in a very few number of products as a colorant; iron oxides are commonly used as colorant in eye-shadows, blushes and concealers (EWG, 2007). On the other hand, at higher concentrations all of the metals are regarded as potentially toxic. Therefore, it is important to measure the accurate concentration of trace metals in the environment.

In order to circumscribe the domain of element speciation, it is mandatory to refer to international union for pure and applied chemistry (IUPAC) recommendation for the definition of terms related to the chemical speciation of elements. Chemical species are specific forms of an element defined as to isotopic composition, electronic/oxidation state,

and complex or molecular structure. While speciation analysis defines the analytical activities of identifying and/ or measuring the quantities of one or more individual chemical species in a sample.

In recent years, trace element speciation has become an important concern in a wide variety of fields; health, environment, food etc. it is no longer a purely academic subject, but various industrial sectors, the government and legislative studies are all involved. The reason for this is that today it has become scientifically proven that mobility, bioavailability, retention, storage and toxicity of trace elements in living systems, food and environment depends on the chemical forms in which it enters the system, the transformations it goes through, e.g. metabolic processes and the final form in which it is present.

The intensive developments in the field of speciation analysis are attributed to the information, the determination of the chemical forms of elements is able to provide, as these determine most of their properties. At the nuclear level isotope distribution can provide information about the geochemical sources of certain elements, while their redox state of elements has a strong influence on properties like solubility and reactivity. At the organometabolic compound level, the nature and number of covalently bound ligands strongly influences the elements properties and at an even higher level of complexity binding layer units such as proteins has a profound influence on factors like mobility, stability, bioavailability and toxicity. Speciation therefore defines the distribution of metals in different forms and provides information on the potential toxicity or essentiality of the investigated sample.

1.2 Statement of Research Problem:

In the last few decades a large amount of heavy metals have been released to the environment through personal care products, medicine, processed foods and fuels. There is however little information on the exposure to metal toxins through consumer/personal care products which are widely used and directly applied to human skin, hence this study.

1.3 Specific Objectives of Research:

The aim of this study is to:

(a) establish the specie form, and concentration of heavy metals such as As, Cr, and Pb in consumer care products and their associated health risks.

The specific objectives of this study are to

(a) determine the species of Cr, As, and Pb in some selected personal care products in Nigeria;

(b) evaluate the concentrations at which these heavy metals exist in the personal care products;

(c) develop the optimum experimental conditions that gives the best recovery for the studied heavy metals in the personal care products; and

(d) specify possible human health risks associated with the species of heavy metals present in the personal care products.

1.4 Scope of the Study

In this study, eleven classes of personal care products that were purchased and analyzed included: powder (Mp3, passion, lillo, ballila and divine), toothpaste (oral B, mymy, olive, close up and longrich), nail removal (teno and lion ail), lip gloss (squeeze & lovely and meidi), soap (septol, lux, kasmo, premier cool, delta and tetmosho), liquid soap (mama