

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

BY

Naheem Oladayo ASAFA

(SCP12/13/H/0040)

B. Sc. (Pure Chemistry), EKSU

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE REQUIREMENTS
OF THE AWARD OF MASTER OF SCIENCE (M. Sc.) DEGREE IN CHEMISTRY TO
THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, OBAFEMI
AWOLOWO UNIVERSITY ILE-IFE, NIGERIA.**

2016

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.

.....
Dr. A. S. Adekunle

(Supervisor)

.....
Date

.....
Dr. J. A. O. Oyekunle

(Co-Supervisor)

.....
Date

.....
Prof. O. O. Soriyaan

(Head, Department of Chemistry)

.....
Date

DEDICATION

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

OBAFEMI AWOLOWO UNIVERSITY

ACKNOWLEDGEMENTS

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.

I also appreciate the fatherly role my Supervisor, and my Co-Supervisor, Dr. Adekunle, A. S. and Dr Oyekunle, J. A. O. respectively played to support me during this study. They encouraged, motivated, and guided me in order not to be misled, I say big thank you Sir. Also to other lecturers in the Department that have really made me to be who I am in the education profession, you have impacted a lot and contributed immensely to my success, I say a big thank you.

To my parents, Mr and Mrs Asafa whom have supported this programme by giving me support financially, morally, and spiritually since the beginning of my life to this moment, I say a big thank you. May Allah reward you abundantly.

I cannot forget to say thank you to my only love, Asheet for her understanding and support before and during this programme. May Allah watch over you for me (Amen).

This acknowledgement will not be completed if I forget to appreciate my brothers, sisters and friends for their supports. You have always been a good ambassador, please continue to be. May Allah reward you abundantly.

OBAFEMI AWOLOWO UNIVERSITY

TABLE OF CONTENTS

Title Page	I
Certification	II
Dedication	III
Acknowledgements	IV
Table of Content	V
List of Tables	X
List of Figures	XII
Abstract	XIII
CHAPTER ONE: INTRODUCTION	
1.0 Introduction	1
1.1 Background to the Study	1
1.2 Statement of Research Problem	3
1.3 Specific Objectives of Research	3
1.4 Scope of the Study	3
1.5 Justification of the Study	4

1.6	Expected Contribution to Knowledge	4
-----	------------------------------------	---

CHAPTER TWO: LITERATURE REVIEW

2.1	Personal Care Products	5
2.2	Hazardous Ingredients in Cosmetics	6
2.2.1	Preservatives	6
2.2.2	Fragrances	7
2.2.3	Heavy Metal Impurities	8
2.3	Regulation for Cosmetics	9
2.3.1	Indian Regulation for Cosmetics	9
2.3.2	European Union Regulation for Cosmetics	10
2.3.3	USA Regulation for Cosmetics	12
2.3.4	Health Canada Regulation for Cosmetics	12
2.4	Heavy Metals	13
2.5	Exposure to Heavy Metal	14
2.6	Human Exposure to Heavy Metal	15
2.6.1	Human Exposure to Chromium	15



2.6.1.1 Respiratory Absorption	16
2.6.2 Human Exposure to Arsenic	17
2.6.3 Human Exposure to Lead	19
2.6.3.1 Gastrointestinal Absorption	20
2.7 Exposure to Heavy Metals through Personal Care Products	21
2.8 Health Effects of Some Heavy Metals	21
2.8.1 Acute Toxicity	22
2.8.1.1 Chromium Acute Toxicity	22
2.8.1.2 Arsenic Acute Toxicity	23
2.8.1.3 Lead Acute Toxicity	25
2.8.2 Neurotoxicity	27
2.8.2.1 Lead Neurotoxicity	27
2.8.3 Genotoxicity	29
2.8.3.1 Chromium Genotoxicity	29
2.8.4 Carcinogenicity	31
2.8.4.1 Chromium Carcinogenicity	31
2.8.4.2 Arsenic Carcinogenicity	33



2.9	Speciation Analysis	35
2.10	Instrumentation Employed in Elemental and Speciation Analysis	37
2.10.1	Atomic Absorption Spectrometry	37
2.10.2	Principle of Atomic Absorption Spectrometry	38
2.10.3	Atomic Fluorescence Spectrometry	40
2.10.4	Atomic Emission Spectrometry	40
2.10.5	Inductively Coupled Plasma Mass Spectrometry	41
2.10.6	Plasma Source Time-of-Flight Mass Spectrometry	42
2.10.7	Glow Discharge Plasmas as Tunable Sources for Elemental Speciation	42
2.10.8	Electrospray Mass Spectrometry	42
2.10.9	Electrochemical Methods	43
2.11	Techniques Employed in Elemental Speciation Analysis	43
2.11.1	Liquid Chromatography (LC)	43
2.11.2	Gas Chromatography (GC)	44
2.11.3	Capillary Electrophoresis (CE)	46
2.11.4	Gel Electrophoresis (GE)	47
2.11.5	Solid-Phase Extraction (SPE)	48

2.11.5.1 Advantages of Solid-Phase Extraction	50
2.11.5.2 Process of Solid-Phase Extraction	52
2.11.5.3 Resins as Solid Sorbents	54
2.11.5.4 Macroporous Resins	56
2.11.5.5 Retention of Trace Elements on Sorbents	60
2.12 Amberlite XAD-16	66
2.12.1 Pretreatment of AmberliteXAD16 Resin	69
3.0 CHAPTER THREE: EXPERIMENTAL	71
3.1 Reagent and Solution	71
3.2 Sample Collection and Preparation	71
3.3 Methodology for the Model Studies	71
3.4 Determination of Total Heavy Metals (Cr, Pb and As)	72
3.4.1 Determination of the Total Metal (Cr, Pb and As) Liquid Sample	72
3.4.2 Determination of the Total Metal (Cr, Pb and As) Solid Samples	73
3.5 Speciation Experiment	73

3.5.1	Column Preparation and Pretreatment	73
3.5.2	Optimization of Some Speciation Parameters	73
3.5.2.1	Effect of pH	73
3.5.2.2	Effect of Eluent Volume	74
3.5.2.3	Effect of Flow Rates	74
3.5.2.4	Effect of Sample Volume	74
3.5.2.5	Effect of the amounts of resin	75
3.5.3	Sample Speciation Experiment	75
3.5.3.1	Chromium (VI) and Lead (IV) speciation Experiment	75
3.5.3.2	Arsenic (III) Speciation	76

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1	Optimization Experiment Results	77
4.2	Recovery Analysis for Heavy Metal Species (As (III), Cr (VI) and Pb (IV)) in Spiked Test Solution.	84
4.3	Total Metal Concentration in the Personal Care Products	88
4.4	The Comparisons Study between the Current Study, Literatures and the Regulatory Standards.	105



CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

5.0	Conclusion and Recommendations	108
5.1	Conclusion	108
5.2	Recommendations	109
	References	110
	Appendix	134

LIST OF TABLES

Table	Caption	Page
2.0	Limits for Heavy Metals in Cosmetic in Indian	11
2.1	Comparisons of LLE, SPE and LC	51
2.2	Some of the Commercially Available Resin Adsorbents	61
2.3	Properties of Amberlite XAD-16	67
2.4	Suggested Operating Conditions	70
4.1a	Percentage Recovery of Arsenic (III) and Arsenic (V) at Different pH and Eluent Concentration	78
4.1b	Percentage Recovery of Lead (II) and Lead (IV) at Different pH and Eluent Concentration	80
4.1c	Percentage Recovery of Chromium (III) and Chromium (VI) at Different pH and Eluent Concentration	81
4.2	Volume of Eluents Studied and the Percentage Recovery of As (III), Pb (IV) and Cr (VI) at pH 3.0, 2.0 and 2.0 Respectively	82

4.3	Flow Rate Studied and the Percentage Recovery of As (III), Pb (IV) and Cr (VI) at pH 3.0, 2.0 and 2.0 Respectively	83
4.4	Volume of Sample Studied and the Percentage Recovery of As (III), Pb (IV) and Cr (VI) at pH 3.0, 2.0 and 2.0 Respectively	85
4.5	Amount of Resin Studied and the Percentage Recovery of As (III), Pb (IV) and Cr (VI) at pH 3.0, 2.0 and 2.0 Respectively	86
4.6	Arsenic (III) Determinations in Spiked Test Solution	87
4.7	Chromium (VI) Determinations in Spiked Test Solution	89
4.8	Lead (IV) Determinations in Spiked Test Solution	90
Table	Caption	Page
4.9a	Arsenic Concentrations in the Personal Care Products	92
4.9b	Chromium Concentrations in the Personal Care Products	97
4.9c	Lead Concentrations in the Personal Care Products	103

4.10 The Comparisons Study between the Current Study, Literatures and the Regulatory Standards	107
--	-----

OBAFEMI AWOLOWO UNIVERSITY

LIST OF FIGURES

Figure	Caption	Page
2.1	Schematic of an Atomic Absorption Spectrometry	39
2.2	Disposable Sorbent Container	49
2.3	SPE Operation	53
2.4	Sorbents Based on Organic Supports	57
2.5	Sorbents Based on Inorganic Supports	58
2.6	Amberlite XAD-16	68



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 HNO₃ 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 (kasmu) 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 (kasmu) 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

OBAFEMI AWOLOWO UNIVERSITY

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, kasmol, premier cool, delta and tetmosho), liquid soap (mama

OBAFEMI AWOLOWO UNIVERSITY