



## QUANTITATIVE ASSESSMENT OF METALS IN SOME ANTIPERSPIRANT FORMULATIONS MARKETING IN NIGERIA

Kasim, L. S.<sup>1\*</sup>, Ogunnubi B.<sup>1</sup>, Dawodu John O.<sup>2</sup>, Olaitan Olatunde J.<sup>2</sup>, Ayodele Olatunde.<sup>2</sup>

<sup>1</sup>Faculty of Pharmacy, Olabisi Onabanjo University, Sagamu, Ogun State, Nigeria

<sup>2</sup>Department Pharmaceutical and Medicinal Chemistry, Olabisi Onabanjo University, Sagamu, Ogun State, Nigeria

\*Corresponding Author Email: kasimls@yahoo.co.uk

DOI: 10.7897/2277-4572.02439

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Received on: 24/04/13 Revised on: 14/06/13 Accepted on: 28/06/13

### ABSTRACT

Antiperspirants are astringent substances applied to the skin to reduce or prevent sweat. The process of sweating is an important, normal physiological process that enables us excrete excess water and salt from the body. However conditions like hyperhidrosis (excessive sweat) led to the need for control of sweat using antiperspirants, although antiperspirants are now used for cosmetic purposes in recent times. This study was conducted to determine the concentration of Aluminium (Al), which is the active ingredient in most antiperspirants and also to determine the presence and concentration of other metals such as Lead (Pb), Cadmium (Cd), Nickel (Ni), Zinc (Zn), and Copper (Cu). Ten (10) brands of antiperspirant samples marketed in Nigeria were purchased. All samples were pre-treated using acid digestion and the concentrations of Al, Pb, Cd, Ni, Zn and Cu were determined using Atomic Absorption Spectrophotometer (AAS)(Perkin Elmer A Analyst 200.Germany). For all the antiperspirant samples analysed, metals such as Cd, Ni, Zn and Cu were not detected while the concentrations of Al and Pb found were between (0.624 – 2.416mg/L) and (1.787 – 5.610mg/L) respectively. In comparison to the standard permissible limits of aluminium in antiperspirants, the percentage of aluminium in all the samples analysed was within the standard permissible limit set by the United States Food and Drug Administration (FDA). Nine samples conformed to over the counter antiperspirants value while one conformed to a prescription antiperspirant value. However, the presence of lead metal in the antiperspirant samples may be a health risk to the consumers.

**Keywords:** Antiperspirants, heavy metals, hyperhidrosis, toxicity.

### INTRODUCTION

Perspiration is a process of sweating; it is an important, normal physiological process that enables us excrete excess water and salt from the body. This process is important to maintain body temperature. An attempt to control sweat with the application of antiperspirants has long been adopted in cases of excessive sweating (hyperhidrosis)<sup>1</sup>.

Antiperspirants are astringent substances applied to the skin to reduce or prevent perspiration. Antiperspirants are often confused with deodorants. While deodorants are substances applied to the body to affect body odour caused by bacterial growth and the smell associated with bacterial breakdown of perspiration in armpits, feet and other areas of the body<sup>2</sup>.

Antiperspirants primarily prevent sweating by affecting sweat glands and can as well as prevent body odour. Thus antiperspirants can be said to be a subgroup of deodorants. In the United States, deodorants are classified and regulated as cosmetics while antiperspirants are classified as drugs by the United State Food Drug Administration (FDA).

Most antiperspirants contain aluminium salts as its active ingredient together with other excipients used in their formulation<sup>1</sup>.

The allowable aluminium salts commonly used include such as Aluminium Chloride, Aluminium Chlorohydrate, Aluminium Chlorohydrate Polyethylene Glycol Complex, Aluminium Chlorohydrate Propylene Glycol Complex, Aluminium Dichlorohydrate, Aluminium Dichlorohydrate Polyethylene Glycol Complex, Aluminium Dichlorohydrate Propylene Glycol Complex, Aluminium Sesquichlorohydrate, Aluminium Sesquichlorohydrate Polyethylene Glycol Complex, Aluminium Sesquichlorohydrate Propylene Glycol Complex, Aluminium Sulfate Buffered, Aluminium Zirconium Octachlorohydrate, Aluminium Zirconium Octachlorohydrate Glycine Complex, Aluminium Zirconium Pentachlorohydrate, Aluminium Zirconium

Pentachlorohydrate Glycine Complex, Aluminium Zirconium Tetrachlorohydrate, Aluminium Zirconium Tetrachlorohydrate Glycine Complex, Aluminium Zirconium Trichlorohydrate, Aluminium Zirconium Trichlorohydrate Glycine Complex, Aluminium Sulfate Buffered With Sodium Aluminum Lactate. Aluminium chlorohydrate and Aluminium zirconium tetrachlorohydrate glycine are the most frequent active ingredients in commercial antiperspirants<sup>3</sup>.

Similar to other drug samples, there is a permissible percentage of aluminium salts allowed in antiperspirants and this is controlled in the United State by the Food and Drug Administration (FDA).The standard percentage of aluminium salt allowed in antiperspirants is between 1 - 25% for over the counter antiperspirants and 25-40% for prescription antiperspirants. The actual quantity present in each antiperspirant varies from brand to brand.

Though heavy metals are not envisaged in antiperspirant preparation but recent studies by researchers have proved this wrong. Toxic metals (lead, cadmium, mercury and arsenic) are widely found in our environment<sup>4</sup>. Humans are exposed to these metals from numerous sources, including contaminated air, water, soil and food<sup>5</sup>. Recent studies indicate that transition metals act as catalysts in the oxidative reactions of biological macromolecules therefore the toxicities associated with these metals might be due to oxidative tissue damage. Redox-active metals, such as iron, copper and chromium, undergo redox cycling whereas redox-inactive metals, such as lead, cadmium, mercury and others deplete cells' major antioxidants, particularly thiol-containing antioxidants and enzymes. Either redox-active or redox-inactive metals may cause an increase in production of reactive oxygen species (ROS) such as hydroxyl radical (HO.), superoxide radical (O<sub>2</sub>.-) or hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Enhanced generation of ROS can overwhelm cells'

intrinsic antioxidant defences, and result in a condition known as “oxidative stress”. Cells under oxidative stress display various dysfunctions due to lesions caused by ROS to lipids, proteins and DNA<sup>6</sup>.

Consequently, it is suggested that metal-induced oxidative stress in cells can be partially responsible for the toxic effects of heavy metals. Heavy metals such as Lead, Mercury, Cadmium, Nickel, Chromium and other toxic organic chemicals or phenolic compounds discharged from pharmaceutical industries are known to affect the surface and ground waters<sup>7</sup> which invariably constitute a health hazards. And due to mutagenic and carcinogenic properties of heavy metals, much attention has been paid to them since they have direct exposure to humans and other organisms<sup>8</sup>. It is not misnomer then to establish the absence of heavy metals in all human products. The present study is aimed at quantifying the amount of metals present in some of the antiperspirant preparations present in Nigeria market.

## MATERIALS AND METHODS

### Chemicals and reagents

All chemicals and reagents were of analytical grade and were obtained from BDH Chemicals Ltd, UK. Concentrated Aqua Regia (mixture of conc. HNO<sub>3</sub> and conc. HCL in ratio 1:3) was used for the digestion of the samples while corresponding metal salts [namely, Pb(NO<sub>3</sub>)<sub>2</sub>, NiCl<sub>2</sub>·6H<sub>2</sub>O and Cr(NO<sub>3</sub>)<sub>3</sub>] were used as standards.

### Instrumentation

AAS instrument (PERKIN ELMER A. Analyst 200; Germany) consisting of a hollow cathode lamp, slit width of 0.7 nm and an air-acetylene flame was used for this work. The samples were analyzed for Aluminium and the heavy metals,

### Samples

Ten (10) brands of antiperspirants marketed in Nigeria were randomly sampled and Purchased from supermarkets in Sango-Ota and Sagamu in Ogun State, Nigeria and they are described as shown in Table 1.

**Table 1. Samples of various brand of Antiperspirant purchased from Commercial Stores**

Samples	B/N	COM	DOM	DOE	DOP
A	Nil	Indonesia	05/08	07/12	10/11
B	0821201	France	05/10	08/14	10/11
C	04120179KV	Nil	09/07	06/12	10/11
D	02761LD	Ireland	10/10	10/14	10/11
E	609	Nigeria	05/11	05/16	10/11
F	10114710	Germany	09/09	06/13	10/11
G	10284LWA	Ireland	10/11	09/15	10/11
H	Nil	England	03/08	01/12	10/11
I	Nil	Canada	09/10	07/14	10/11
J	902	Taiwan	11/10	10/15	10/11

Batch number (B/N), Country of manufacture (COM), Date of manufacture (DOM), Date of Expiration(DOE) and Date of purchase (DOP)

### Standard Preparation

Calibration plots were obtained using a series of varying concentrations of the standards for all two metals Al and Pb

and were linear with a correlation coefficient of approximately one Figure 3 and 4 respectively. The standard solutions of aluminium and lead used in the calibration plot were prepared by graded dilution of the stock standards. The dilute standards and a reagent blanks were prepared and measured from Atomic Absorption Spectrophotometer (Perkin Elmer A Analyst 200, Germant) for the linear regression curve for each metal.

### Sample Preparation

This was carried out according to official method<sup>9</sup>. 2ml of each brand was digested using 10ml of conc. Aqua regia (combination of Nitric Acid and Hydrochloric Acid in the ratio 1:3). The mixture was evaporated on a hot plate in a fume cupboard until the brown fumes disappeared leaving white fumes.

The digest was allowed to cool and transferred into a 25ml volumetric flask, volume was adjusted to mark with deionized water. The mixture was filtered using filter paper (Whatman filter paper 11mm) into a sample bottle.

The absorbance of aluminium and lead in each sample were determined in the obtained clear solutions using Atomic Absorption Spectrophotometer and the concentration extrapolated from the standard plot (Figure 3 and 4) for each metal. The procedure was repeated twice and the concentration was taken in duplicate as shown in Table 2.

### Data Analysis

Data are expressed as Mean  $\pm$  SD while Students' 't' test with 95% confidence level was used for statistical analysis of the results.

## RESULTS

**Table 2. Concentrations of Metals (mg/l) in Antiperspirant Samples**

SAMPLE	Al		Pb	
	1st	2 <sup>nd</sup>	1st	2nd
A	2.414	2.418	1.789	1.785
B	0.960	0.962	3.408	3.408
C	0.889	0.893	3.579	3.581
D	1.431	1.427	4.580	4.580
E	0.935	0.935	4.683	4.691
F	0.808	0.808	4.593	4.589
G	1.447	1.445	5.401	5.417
H	0.677	0.677	5.381	5.381
I	0.879	0.869	5.561	5.573
J	0.622	0.626	5.610	5.610

**Table 3: Mean Concentrations of Metals (mg/l)  $\pm$  SEM and Percentage of Aluminium and Lead in Antiperspirant Samples**

Sample	Al	Pb	Al (%)	Pb(%)
A	2.416 $\pm$ 0.170	1.787 $\pm$ 0.386	10	7
B	0.961 $\pm$ 0.170	3.408 $\pm$ 0.386	5	17
C	0.891 $\pm$ 0.170	3.580 $\pm$ 0.386	7	27
D	1.429 $\pm$ 0.170	4.580 $\pm$ 0.386	36	115
E	0.935 $\pm$ 0.170	4.687 $\pm$ 0.386	5	23
F	0.808 $\pm$ 0.170	4.591 $\pm$ 0.386	12	69
G	1.446 $\pm$ 0.170	5.409 $\pm$ 0.386	7	27
H	0.677 $\pm$ 0.170	5.381 $\pm$ 0.386	3	27
I	0.874 $\pm$ 0.170	5.567 $\pm$ 0.386	4	27
J	0.624 $\pm$ 0.170	5.610 $\pm$ 0.386	3	28

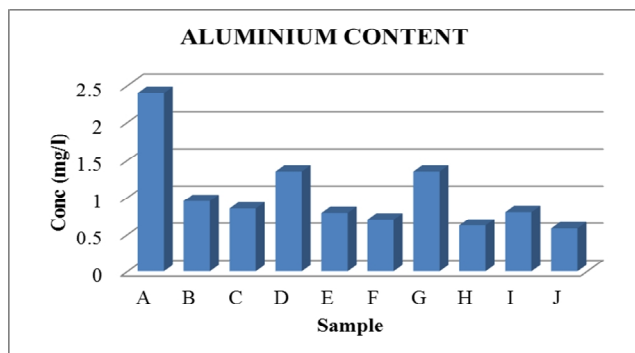


Figure 1: Aluminium Content in Antiperspirant Sample A to J Studied

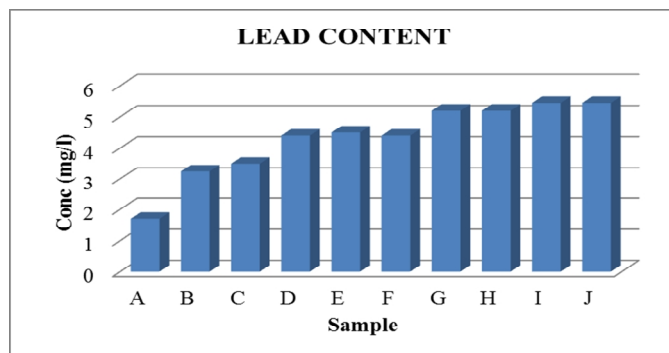


Figure 2: Lead Content in Antiperspirant Sample A to J Studied

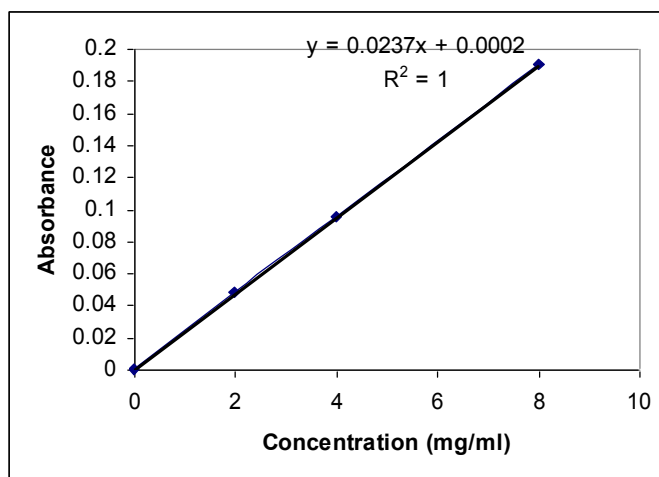


Figure 3: Calibration Plot of Aluminium Standard

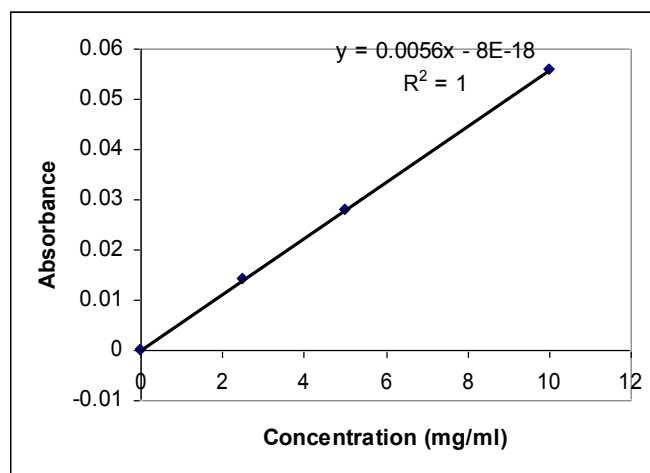


Figure 4: Calibration Plot of Lead Standard

## DISCUSSION

Ten brands of antiperspirants marketed in Nigeria were subjected to quantitative analysis of heavy metals content (Al, Pb, Cd, Ni, Zn and Cu) using Atomic Absorption Spectrophotometer. For all the antiperspirant samples analysed, metals such as Cadmium (Cd), Nickel (Ni), Zinc (Zn) and Copper (Cu) were not detected. Aluminium (Al) and Lead (Pb) concentrations in the antiperspirant samples studied ranges between 0.624 to 2.416mg/L or 3% to 36% (fig 1) and 1.787 to 5.610mg/L or 7% to 115% (Figure 2) respectively and also as shown in Table 3.

Similar to drug samples, there is a permissible percentage of aluminium salts allowed in antiperspirants. The United State

Food and Drug Administration (FDA) set permissible limit for aluminium in antiperspirants as between 1 - 25% for over the counter antiperspirants and 25-40% for prescription antiperspirants. From Table 2, when the result obtained was compared with the standard percentage of aluminium allowed in antiperspirants, nine (9) out of ten (10) of the antiperspirant samples analysed can be said to be over the counter products because the percentage of aluminium content in them ranges from 3% to 12%, while the remaining one (1) sample is a prescription product as its aluminium content is 36%. The percentage of aluminium in all the samples analysed was within the standard permissible limit

set by the United States Food and Drug Administration (FDA).

Table 1 and 2 shows the concentration of Lead (Pb) in the antiperspirant samples studied to range between 1.787 – 5.610mg/L or 7% - 115%. Lead is a toxic metal and should not be present in antiperspirants according to the United States Food and Drug Administration (FDA). Lead is one of the four heavy metals that are of particular concern to human health<sup>10</sup>. It is highly toxic and can cause damaging effects even at very low concentrations. The Department of Health and Human Services (DHHS) has determined that lead acetate and lead phosphate may reasonably be anticipated to be carcinogens based on studies in animals. According to the Occupational Safety and Health Administration (OSHA) of the United States Department of Labour, lead exposure both acute (a few days) and chronic (several years) adversely affects numerous body systems and causes many forms of health impairment and disease. The OSHA states that: "The frequency and severity of medical symptoms increases with the concentration of lead in the blood. Lead causes injuries to mental development which manifest as reduction of intelligence, growth disturbances, spasticity and severe kidney damage. The possibility of Pb substituting for calcium in bone could lead to skeletal abnormalities in children<sup>11,8,12</sup>. Growing children and foetus are particularly at risk of Pb consumption and some plants parts toxicity have been attributed to Pb<sup>13</sup>. Antiperspirant use has been implicated as a risk factor for breast cancer in Iraq<sup>14</sup> and this could be attributed to the presence of Pb and not the Aluminium alone as it is being reported by the other researchers<sup>15,16,3</sup>.

In view of the result obtained from the study, the concentrations of aluminium in the antiperspirant samples are within the standard permissible limit. However, the presence of lead metal in the antiperspirant samples may be a health risk to the consumers.

Therefore, more studies aimed at determining the concentration of heavy metals in other brands of antiperspirants marketed in Nigeria needs to be done to ascertain their safety. Also, materials and consumer products that provide significant exposure, such as air fresheners, lip sticks etc, should be closely monitored to avoid heavy metal poisoning.

#### ACKNOWLEDGEMENT


We hereby acknowledge the contribution of Staff of the department of Pharmaceutical and Medicinal Chemistry, University of Lagos Nigeria for

the provision of standard samples for the experiment. We do also acknowledge the contribution of other staff that assisted in one way or the other.

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Source of support: Nil, Conflict of interest: None Declared

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#### How to cite this article:

Kasim, L. S., Ogunnubi B., Dawodu John O., Olaitan Olatunde J., Ayodele Olatunde. Quantitative assessment of metals in some antiperspirant formulations marketed in Nigeria. *J Pharm Sci Innov.* 2013; 2(4): 1-4.