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Heavy metal assessment of some ceramic products imported into Nigeria from China

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ABSTRACT

Traditional pottery imported from china or other countries may be improperly glazed, and the glaze used to make the pottery may contain large amounts of lead and other heavy metals. Chinese Ceramic wares were randomly selected from products available in the shops at Zaria, Kano and Kaduna markets in Nigeria, and analyzed to determine the levels of heavy metals (Pb, Cd, Ni, Cu, Zn, Cr, Co, and Mn) in the products. All the ceramic wares contain heavy metals in varying concentrations. The results ranged from 218.83-866.67 μgg^{-1}, 21.67-55.00 μgg^{-1}, 155.00-778.00 μgg^{-1},163.33-548.33 μgg^{-1}, 2233.33-6500.00 μgg^{-1}, 111.67-436.67 μgg^{-1}, 250.00-835.00 μgg^{-1}, 2533.33-6783.33 μgg^{-1} for Pb, Cd, Ni, Cu, Zn, Cr, Co and Mn respectively. About 60% of the ceramic ware shows Pb concentration higher than 500 μgg^{-1} recommended by USFDA (1988) whereas Cadmium levels are generally low being less than 60 μgg^{-1}. With the observed high levels of heavy metals in the ceramics used in this study, it is possible that acidic substances can easily induce leaching of these metals.

Keywords: Heavy metal; Ceramics; Leaching.

INTRODUCTION

Ceramics may be considered to be material made from naturally occurring clay or earth. Scientifically, ceramics are compounds of metallic and non-metallic elements. In modern applications, a broader definition applies to the term ceramics that is everything that is not a metal or organic material. Ceramics are inorganic as well as non-metallic materials which have been processed or used at high temperatures [1]. Historically, lead glazes were used in the production of ceramic ware to protect the surface and enhance durability. Glazes added luster and beauty as well. When properly prepared and sealed, lead glazes pose no health threat. However, any lead glazed dish can become toxic if it is fired incorrectly or if it becomes damaged. Lead "leaches" from the vessel into the food or liquid that it contains. Heating the utensil increases leaching, as does acidic food or drink [2].

Imported dishes can present human health hazards in two ways: (1) dinnerware that contains toxic metals in excessive amounts may gain entry to Nigeria; and (2) imported decorative ceramic plates may be improperly labeled regarding permissible use with food. Traditional pottery imported from china or other countries may be improperly glazed, and the glaze used to make the pottery may contain large amounts of lead. Lead can leach out of this type of pottery if it is used to hold or store foods. Traditional pottery used in cooking may poison entire families. Ceramics and other household products have been reported to contain heavy metals [3].

The term heavy metal refers to chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4^0C (39^0F). Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 [4]. Therefore, the elements that are of concern include lead, cadmium, chromium, zinc, nickel, copper etc. These metals may be released into the environment from metal smelting and refining industries, scrap metal, plastic and rubber industries, various consumer products and from burning of waste containing these elements. On release to the air, the elements travel for large distances and are deposited into the soil, vegetation and water depending on their density. Once deposited, these metals are not degraded and persist in the environment for many years poisoning humans through inhalation, ingestion and skin absorption. Acute exposure leads to nausea, anorexia, vomiting, gastrointestinal abnormalities and dermatitis. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time compared to the chemical’s concentration in the environment.

Dinnerware decorated with overglaze designs can release toxic metals into food substances in amounts high enough to constitute health hazards. In a study conducted by Ralph, 1999 [5], non-random samples of dishes were purchased in new condition in US retail outlets and subjected to 24-h acid leaching tests. Two of 28 patterns of imported ceramic dinnerware were found to release lead in levels that exceed US Food and Drug Administration (FDA) limits, and 10 other patterns released lead in concentrations exceeding California Proposition 65 (CA 65) limits. One imported ceramic dish released cadmium in excess of FDA limits. Samples of new foreign-made melamine (plastic) dinnerware in four patterns released neither lead nor cadmium in detectable concentrations.

Samples of porcelain dinnerware manufactured in five European and three Asian countries before the mid-1970s were subjected to acid leaching tests to investigate the release of heavy metals. Forty-six dishes decorated with decals or hand painted designs applied over the glaze were examined. Included in the selection were dishes from major manufacturers of fine dinnerware (Haviland Limoges, Rosenthal, Noritake) as well as samples from lesser-known or unidentified factories. During 24-hour tests with 4% acetic acid, half of the samples (23 dishes) released lead in concentrations exceeding the US Food and Drug Administration (FDA) allowable maximum of 3.0 μg/ml and another 17 dishes released lead in concentrations ranging from 0.1 to 2.9 µg/ml. Five dishes released cadmium, but only one value exceeded the FDA limit of 0.5 µg/ml. Zinc, cobalt, copper and chromium were also released by some of the dishes [6].

Heavy metals have mostly been studied in soil, water, paints, and food [7],[8],[9]. Ceramic wares have not really been investigated as one of the sources of lead, cadmium and other heavy metals. Moreover, a number of imported ceramic chinese dishes used in storing and serving foods have been reported to be a potential lead hazard [10] but no work has been done in Nigeria to investigate the problem. This study was designed to ascertain the levels of lead, cadmium, chromium, nickel, zinc, copper, cobalt and manganese in ceramic wares such as plates, spoons, pots, saucers, cups, tiles, mortal, and flower vex. The ceramic samples were collected from Zaria, Kano, and Kaduna markets in Nigeria.

MATERIALS AND METHODS

Ceramic samples were ground into fine powder and homogenized in a cryogenic mill. Grounded ceramic samples were sieved with 325µm sieve before analysis. All metallic determinations from ceramic samples were based on the fine particles obtained. The procedure for digestion of ceramic samples was based on EPA 3052. The entire item including the glaze, decoration and ceramic base material was grounded in a cryogenic mill and 1g of the grounded ceramic powder was weighed into a 250ml Pyrex beaker for acid digestion. Analar grade Nitric acid and Hydrofluoric acid were used for digestion in an open vessel.

The digest was filtered through a Whatman 41 filter paper to remove the insoluble particles and brought to a final volume of 50ml with deionized water. Blank sample was also prepared similarly. Glass wares, crucibles and plastic containers were washed with liquid soaps, rinsed with distilled water and soaked in 10% HNO_3 for 24hours; cleaned with distilled-deionized water and in such a manner that no contamination occurred [11]. Standards were prepared with serial dilution technique within the range of 0.5-2.5ppm for Lead, Cadmium, Nickel and Manganese, 1-5ppm for Copper and Cobalt, 0.5-2ppm for Zinc and 2-10ppm for Chromium. The instrument was first calibrated with stock solutions of the prepared standards before analysis. The final processed samples were quantitatively analyzed using Buck Scientific VGP 210 Flame Atomic Absorption Spectrophotometer. After every five samples analyzed using AAS, the first sample was repeated for quality check. Only when the results were within 10% of earlier readings did the analysis proceed further.

RESULTS AND DISCUSSION

The results of heavy metals concentration in the ceramic samples are presented in Table 1. All the ceramic wares contain heavy metals in varying concentrations. The results ranged from 218.83-866.67 μgg^{-1}, 21.67-55.00 μgg^{-1}, 155.00-778.00 μgg^{-1},163.33-548.33 μgg^{-1}, 2233.33-6500.00 μgg^{-1}, 111.67-436.67 μgg^{-1}, 250.00-835.00 μgg^{-1}, 2533.33-6783.33 μgg^{-1} for Pb, Cd, Ni, Cu, Zn, Cr, Co and Mn respectively. The concentration of essential elements like Zn and Mn are significantly higher than that of non-essential toxic metals like Pb, Cd, Ni and Cr in the samples. Zinc and Manganese are not of toxicological significance. Zinc has an established role as surface pigment in paints. Evidence shows that it is important as an essential nutrient necessary for catalytic function of specific enzymes. Zinc participates in all major biochemical pathways and

Table 1: Mean (±SD) heavy metal concentration (ugg^{-1}) in Ceramic wares

Samples	Metals							
	Pb	Cd	Ni	Cu	Zn	Cr	Co	Mn
Saucer	218.83±10.41	21.67±2.89	640.00±109.67	205.00±8.67	6166.67±189.30	125.00±25.00	736.67±12.58	6783.33±500.83
Flower Vex	578.33±72.34	38.33±7.64	706.67±30.14	335.00±8.67	5783.33±436.85	166.67±28.87	835.00±43.59	3500.00±100.00
Cup	558.33±7.64	51.67±2.89	778.33±2.89	205.00±5.00	3766.67±125.83	398.33±7.64	281.67±10.41	3833.33±57.74
Tiles	618.33±50.08	55.00±5.00	666.67±7.64	241.67±2.89	3150.00±150.00	436.67±10.41	276.67±5.77	5065.00±31.22
Plate	295.00±18.03	16.67±2.89	555.00±21.79	548.33±10.41	2233.33±160.73	303.33±10.41	331.67±577	2533.33±115.47
Pot	398.33±32.53	33.33±2.89	265.00±30.41	251.67±7.64	6500.00±100.00	258.33±18.93	250.00±10.00	3483.33±76.38
Spoon	866.67±23.63	33.33±12.58	155.00±22.91	163.33±10.41	5016.67±104.08	111.67±12.58	395.00±5.00	3566.67±57.74
Spoon	751.67±62.92	41.67±5.77	311.67±5.77	313.33±2.89	5735.00±239.11	203.33±5.77	413.33±2.89	3733.33±448.14

Table 2: Duncan's one way Analysis of Variance (ANOVA) of Means for heavy metal concentration (ugg^{-1}) in Ceramic samples

Metals	Samples							
	Saucer	Flower vex	Cup	Tiles	Plate	Pot	Spoon	Mortal
Pb	218.33^{a}	578.33^{b}	558.33^{b}	618.33^{b}	295.00^{c}	398.33^{d}	866.67^{e}	751.67^{f}
Cd	21.67^{a}	38.33^{b}	51.67^{cd}	55.00^{c}	16.67^{a}	33.33^{b}	$33.33^{\mathbf{b}}$	41.67^{f}
Ni	640.00^{a}	706.67^{ab}	778.33^{b}	666.67^{a}	555.00^{c}	265.00^{d}	155.00^{e}	311.67^{d}
Cu	205.00^{a}	335.00^{b}	205.00^{a}	241.67^{c}	548.33^{d}	251.67^{c}	163.33^{e}	313.33^{b}
Zn	6166.67^{a}	5783.33^{b}	3677.67^{c}	3150.00^{d}	2233.33^{e}	6500.00	5016.67	5735.00
Cr	125.00	166.67	398.33	436.67	303.33	258.33	111.67	203.33
Co	736.67	835.00	281.67	276.67	331.67	250.00	395.00	413.33
Mn	6783.33	3500.00	3833.33	5065.00	2533.33	3483.33	3566.67	3733.33

($P<0.05$); Means with the same superscript in the same row are not significantly different

Table 3: Correlation among heavy metals in Ceramics

	Pb	Cd	Ni	Cu	Zn	Cr	Co	Mn
Pb	1							
Cd	0.579	1						
Ni	-0.420	0.250	1					
Cu	-0.402	-0.474	0.144	1				
Zn	0.044	-0.104	-0.377	-0.469	1			
Cr	-0.079	0.577	0.480	0.159	-0.685	1		
Co	-0.183	-0.307	0.307	-0.024	0.472	-0.654	1	
Mn	-0.297	0.048	0.309	-0.546	0.302	-0.129	0.378	1

plays multiple roles in the perpetuation of genetic material, including transcription of DNA, translation of RNA, and ultimately cell division [12]. Thus the observed high values of these metals may not indicate any present possible health hazard. Cadmium levels are generally low being less than 60 μgg^{-1}. About 60% of the ceramic ware shows Pb concentration higher than 500 μgg^{-1} recommended by USFDA (1988) [13]. Jonathan and Flora (2005) [14] analyzed ceramic ware and reported Pb concentrations of 630 μgg^{-1} and 560 μgg^{-1} for saucer and cup respectively. These values are comparable to the values obtained in this study.

Analysis of variance (ANOVA) (Table 2) showed significant variations ($P<0.05$) between ceramic samples for the heavy metals determined. There is significant variation in the levels of Zn, Cr and Co in the samples. The concentration of Pb in saucer (218.33 μgg^{-1}) is significantly different from that of Tiles (618.33 μgg^{-1}) and spoon (866.67 μgg^{-1}). However, there is no significant difference between concentrations of Nickel in saucer, Flower vex, Cup and Tiles. Pearson correlation among heavy metals in the ceramic samples was calculated to see if some metals were interrelated with each other and the results are presented in Table 3. Correlation study of the data indicated a relatively weak correlation between Pb and Cd (0.579); Cd and Ni (0.577), Ni (0.250); Ni and Cr (0.480), Co (0.307), Mn (0.309). The negative correlation observed in most of the metals shows that the metals are probably not from the same source and the presence of one does not necessarily indicate the presence of the other.

With the observed high levels of heavy metals in the ceramics used in this study, it is possible that acidic substances can easily induce leaching of these metals since the solubility of Pb increases with decrease in pH value (Jonathan and Flora, 2005.). Consequently, food items and beverages prepared in such ceramic ware, are likely to show high levels of Lead.

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