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Determination of Some Heavy Metals from Domestic Ceramic Products Used In Kaduna, Nigeria

IDRIS M.K[1,2], OYEWALE A O[2], HAUWA M.S.H[1]

[1]Dept of Applied Science, C S T, Kaduna Polytechnic, Kaduna
[2]Dept of Chemistry Nigerian Defence Academy, Kaduna

Abstract: **Levels of heavy metals: lead, chromium, manganese, zinc, copper and cadmium which were incorporated as glazes in the production of ceramic wares were analyzed in different ceramic materials using atomic absorption spectrophotometric method. The ceramic materials analyzed were spoon, pot, soup bowl, plate, mug and cup. Atomic absorption spectrophotometric analysis of the ceramic wares sampled revealed varying concentrations of these metals. The results obtained for the six metals in six ceramic samples ranged between 13.7075 mg/kg and 140.905mg for lead; 101.565 and 233,01 mg/kg for chromium, 0.1325 and 3.63 mg/kg for cadmium; 44.3325 and 1449.047 mg/L for manganese; 61.0625 and 1033 mg/kg for zinc; and 0.2350 and 6.260 mg/kg for copper. The levels of lead, manganese, zinc, chromium and copper in all the wares analyzed were above the permissible limits while the levels of chromium in all the wares analyzed with the exceptions of mug were above the permissible limits of World Health Organization (WHO) and Society of Glass and Ceramic Decorators. The result implies that the continuous domestic use of these wares pose potential danger to the end user. Consumption of food and drinks from these ceramic wares has attendant health implications owing to the toxicity of these metals, which could include; kidney and liver damage, loss of appetite, insomnia, chest pain, diarrhea, renal dysfunction, pneumonia and impotence in both men and women. The results were subjected to Pearson correlation analysis to see if some metals were interrelated with each other. The negative correlation observed between these metals indicated that the metals were probably not from the same source and that the presence of one does not affect the presence of other significantly. Similarly, the positive correlation between the metals indicated that they may probably be either of the same source or that the presence of one may affect the other.**

Keywords: **Ceramic, heavy metals, leaching, permissible limits.**

1. INTRODUCTION

Ceramics may be considered to be material made from naturally occurring clay or earth material. Scientifically, ceramic materials are inorganic, non metallic materials made from compounds of a metal and non metal. Ceramic material may be crystalline or partly crystalline (wikepedia.2012). Most traditional ceramic products were made from clay (or clay mixed with other materials) shaped and subjected to heat. Table wares and decorative ceramics are generally still made using the same method (wikepedia.2012).

Historically, ceramic art mean art objects such as figurines, tiles and table ware made from clay by the process of pottery. Some ceramic products are regarded as fine arts while others are regarded as decorative, industrial or applied art objects, or as artifacts in archeology (wikepedia.2012). Ceramic materials tend to be strong, stilt, brittle, chemically inert, and non conductors of heat and electricity but their properties vary widely. Ceramic generally can withstand very high temperatures such as temperatures that range from 1,000 to 1,600^{o}C (1,800 F to 3,000 F). 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 [Omolaoye et al.,2010]. Most table ware manufacturers use unleaded glazes when producing table wares patterns, but design requirements occasionally mandate the use of decorative borosilicate enamels containing some heavy metals

(Mary,2007). The incorporation of heavy-metal borosilicate enamels in ceramic products brings out to the fore heavy metals in ceramic materials viz-a-viz the health implication therein. However, lead glazes pose no health threat when properly prepared and sealed but can become toxic if it is fired incorrectly or if it becomes damaged. Lead is added to the glaze in order to lower the baking temperature and make ceramic articles more usually attractive. If ceramic articles are baked at the wrong temperature, the glazing will not have the desired sealing properties and lead can leak into food and drinks with a low pH (Panel on food additives,2004).

2. EXPERIMENTALS

2.1 *Sample Collection:*

Ceramic samples in the form of cup, mug, soup bowl, plate, spoon, and pot were all randomly selected from available products and purchased from Kaduna Central Market (Sheik Gumi Central Market).The ceramic Plate were made from stoneware ceramic company; cup and spoon were made from S.M.P ceramic company while soup bowl, pot and mug were made from EMEL and Seammi ceramic companies respectively, all of which were ceramic companies based in China where the products were imported.

2.2 *Sample Preparation:*

Ceramic samples were crushed and grounded into fine powder using cell cylindrical steel metal (pistil and mortar) which is used for the grinding of hard materials. The cell was thoroughly washed and dried to avoid contamination. The ground samples were sieved using sieve of 250 µm size. The whole of the sample material including glaze decoration and ceramic base material were crushed and grounded to obtain homogeneity. The powdered samples were kept in a clean dry plastic container prior to analysis.

2.3 *Samples Digestion:*

To each sample (2 g) in a beaker, 10 cm^3 of 60 % hydrofluoric acid, 10 cm^3 of Conc. Nitric acid and 1 cm^3 of conc. H_2SO_4 was added. The beaker was covered to allow the reaction subside for 5-6 mins. The content was then heated to between 50-60 ^OC for 15 mins on hot plate and stirrer in fume cupboard because of the appearance of NO_2. The mixture was then heated on a water bath for 75 mins at temperature of about 110 ^OC until the contents of the beaker were reduced to few centimeters. The digest was allowed to cool and filtered through Whatman 41 filter paper into 50 cm^3 graduated plastic bottles. The filtrate was diluted to the mark using distilled water (Parkinson and Christopher,1974) Each sample was digested using the same procedure and was analysed using AAS.

3. PREPARATION OF STOCK SOLUTIONS

Working standards were prepared for each metal by serial dilution of the stock solutions of the respective elements prepared. Working standard of 0.5-2.5 ppm for manganese, cadmium and lead, 1-5 ppm for copper and 0.5-2 ppm for chromium and zinc were prepared.

All glass wares and plastic containers used were first washed using detergent and soaked in 10 % HNO_3 acid for 2 hours, cleaned with distilled and dried to avoid contamination.

4. RESULTS

The results of the analysis of heavy metals in ceramic materials using Atomic absorption sphectrophotometry is presented in Table 1 below.

Table 1: Heavy metal concentrations in ceramic wares digests (mg/kg)

Samples	Pb	Cr	Cd	Mn	Zn	Cu
Pot	32.3775	101.565	0.4125	47.25	1033.3675	2.3375
Soup bowl	140.905	175.6825	1.1400	88.4125	61.0625	0.2350
Plate	67.420	86.7575	3.630	44.3325	1603.8475	0.6875
Cup	134.0175	148.610	0.6925	1449.047	123.6775	4.2975
Mug	13.7075	213.6975	0.1325	44.970	90.4275	6.2600
Spoon	119.1925	233.010	0.335	201.7775	110.7775	5.055

All the results obtained and presented were the average for the triplicate determinations of the samples digests.

Table 1 show the results of the analyses of metals in ceramic materials ranged between 3.630 and 0.1325 mg\kg for Cd; 140.905 and 13.7075 mg/kg for Pb ; 233 and 86.7575 mg/kg for Cr ; 1449.0425 and 44.3325 mg/kg for Mn;1603 and 61.0625 mg/kg for Zn and 6.2600 and 0.2350 mg/kg for Cu. The level of Pb was highest in the soup bowl and lowest with the mug. Chromium level was found to be highest in spoon and lowest in the pot samples while Zn was highest in plate and lowest in soup bowl

Table 2: Correlation Matrix and Pearson Correlation among Heavy Metals

	Pb	Cr	Cd	Mn	Zn	Cu
Pb	1.00					
Cr	.208 (.692)	1.00				
Cd	.047 (.930)	-643 (.169)	1.00			
Mn	.505 (.306)	-0.023 (.966)	-.171 (747)	1.00		
Zn	.417	-.0853 (.031)	.758 (.080)	-.334 (.518)	1.00	
Cu	.085 (.873)	.541 (0.268)	-6.22 (.187)	.488 (.326)	-.479 (.377)	1.00

(γ=0.05)

Table 2 showed the correlation analysis between the analysed metals in the ceramic material analysed. High positive correlation is observed between Pb and Cd (r= 0.930) while the lowest correlation among metals is between Cu and Cr (r= 0.085). Then the negative correlation was observed between Cd and Cr; Mn and Cr; and Cu and Zn.

5. DISCUSSSION

The results of trace metals analyzed in six ceramic materials were presented in Table 1. The results indicated the varying concentrations of trace metals in different ceramic materials wares analyzed.

The result for Pb for all the ceramic wares obtained were above the permissible limit of [WHO GUIDLINES], Society of Glass and Ceramic Decorators (2004) and Norwegian scientific committee for Food Safety for Ceramic Wares. The results is consistent with the results of a survey conducted in 2004 by Panel on food additives, flavouring, processing aids and materials in contact with food and cosmetics. The range of the Pb concentrations observed in this study was as observed and reported by (Society of glass ceramic decorators,1998).

The results for the Cd in all the ceramic wares analyzed with exceptions of mug were above the permissible limit of WHO and Society of Glass and Ceramic decorators. The highest was recorded in plate while the lowest was in mug.

The results of Cr determined and presented in Table 1 for all the ceramic wares analyzed were above the FAO/WHO permissible limits of 2.3 mg/L of Cadmium in foods. Spoon and Mug showed the highest concentration of 233.01 mg/KG and 213 mg/KG respectively. The results were close to the values of concentration of Cr obtained in ceramic wares by (Carmen et al.,2011) and (Ajmal et al.,1997). This indicates that these material when used domestically may likely leach chromium into foods in high concentrations and thus if consumed may lead to chromium poisoning.

The results for the Cu obtained for all the materials analyzed were within the permissible limit of WHO of 2 mg/L for drinking water and 10 mg/L in all food, a standard set by CAC (2013). The results of Cu concentration obtained were as reported by [Yusuf et al.,2006] in the study of heavy metals leached from ceramic wares.

The results of Zn obtained in all ceramics analyzed exceeded the permissible limits of 60 mg/kg set by FAO/WHO. The highest value was recorded in pot (1033 mg/kg.36) (Jerzy et al.,1998) reported 6166 mg/kg as the highest concentration of Zn in the analysis of heavy metals in ceramic materials imported from china.

The concentrations of Mn detected in all the ceramic wares analyzed were above the limit set by WHO of 0.5 mg/L in foods. Cup showed a high value of 1449 mg/kg. Ajmal et al.,(1997) reported a range of Mn between 135-853 mg/l while Yusuf et al.(,2006) reported concentrations of Mn ranged between 2533--6783 mg/kg. This indicates a uniformity of data from the analysis of heavy metals in ceramic materials. The high concentration of Mn in all these materials indicated the propensity with which it can easily be leached into foods within a reasonable contact time thereby exposing one to the dangers of manganese poisoning.

6. CONCLUSION

Heavy metals in the form of borosilicates are incorporated as glazes in the production of ceramic domestic wares. Levels of these heavy metals (lead, chromium, manganese, zinc, cupper and cadmium) were analyzed in different brands of ceramic domestic wares (spoon, pot, cup, plate, soup bowl and mug) using AAS method. The results indicated that the levels of lead, chromium, manganese, zinc and copper in all the wares analyzed were above the permissible limits of WHO and society of glass and ceramic decorators. The levels of chromium in all levels the wares analyzed were found to be above the permissible limits of WHO and society of glass and ceramic decorators with the exception of ceramic mug were within the permissible limits of WHO.

The study of the Pearson correlation of the data did indicate a week correlation among the metals analyzed while t-test analysis of the data showed no significant differences in the concentration of heavy metals leached between the leachant solutions used.

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