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RESEARCH ARTICLE

High level leaching of heavy metals from colorful ceramic foodwares: a potential risk to human

Taiwo Adedoyin Aderemi[1] · **Adeniyi Abiodun Adenuga**[1] · **John Adekunle Oyedele Oyekunle**[1] · **Aderemi Okunola Ogunfowokan**[1]

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Abstract Ceramic foodwares are among the products used by people on daily basis without being cautious of exposures to heavy metals through possible leaching from the glaze ceramics. This study investigated the levels of heavy metals found in some commonly used ceramic foodwares in Nigeria with the aim of determining levels of human exposures through the use of the ceramics. To achieve this, acid digestion was carried out for the total metal concentrations and leaching tests were done using 4% acetic acid as a leaching agent. Metal concentrations were quantified using flame atomic absorption spectrometry (FAAS) and particle-induced X-ray emission spectrometry (PIXES) analysis. All the ceramic foodwares studied were found to contain varied amounts of heavy metals in their glazes, with concentrations in the range of 26.45–2071.46, 5.20–547.00, 1.24–2681.02, 2590.00–8848.40, 6.42–654.66, 112.69–649.95, 63.38–2518.51, and 3786.51–8249.44 $\mu g\ g^{-1}$ for Pb, Cd, Zn, As, Cu, Cr, Mn, and Fe, respectively. Concentrations of the metals leached from the ceramics were in the range of 0.11–0.97, 0.01–0.28, 0.00–4.19, 1.93–15.00, 0.01–0.41, 0.09–0.60, 0.01–2.14, and 0.01–11.53 mgL^{-1} for Pb, Cd, Zn, As, Cu, Cr, Mn, and Fe, respectively. Comparing the ratio of the metals leached from the ceramic wares with those of the metal oxides in the ceramics, it was noticeable that not all the metals detected in the ceramic samples were domiciled in the glaze but in the clay materials used for the ceramics.

Keywords Ceramic foodwares · Heavy metals · Leaching · Safety · Adverse effects

Introduction

The exponential increase in the use of heavy metals in various industrial processes for the production of regularly used household materials is a huge concern for possible human exposure to potentially toxic metals. Exposure of humans to heavy metals has been observed to rise continuously through consumption of contaminated diet and water and as a result of contamination coming from unforeseen sources like the food storage containers and dishwares. The use of ceramic foodwares is widespread across the length and breadth of the globe. In Nigeria, there is an increase in the amount of both locally made and imported ceramic foodwares of varied types and sizes entering the markets on regular basis, most of which lacked information about the important compositions and place of production, thus making it difficult to ascertain the safety of their use. Notwithstanding, since there is little or no regulation in place, the importer or manufacturer of such products is let free to flood the market with questionable quality and safety compromised ceramic foodwares. Ceramic foodwares are important commodities in Nigeria, and they are gaining more acceptance by people of all social status, especially the colorful ones, which are the preferred for use at major functions and events to serve foods and drinks. Considering the country's population of over 150 million, it is estimated that Nigeria currently spends about five billion Naira annually on importing ceramic products; the global ceramic market is forecast to reach 408 billion dollars by 2018 with China as a key player (*Nigeria Punch Newspaper* 2015).

Ceramics possess various advantages that made them to be well acceptable for use at home, commercial kitchens, and

Responsible editor: Philippe Garrigues

✉ Adeniyi Abiodun Adenuga
adenugaa@oauife.edu.ng

[1] Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

social functions; they are corrosion-resistant, good insulators that can withstand high temperature, are easy to clean, are hard but brittle, and usually come with adorable coloration. Glazes are applied to clay-based ceramic products to provide a protective finish and a shiny and smooth surface for a porous clay object and to incorporate enticing coloration (Turbett and Stephenson 1978; Belgaied 2003). Historically, heavy metals like lead, cadmium, and others are in glazes used in the production of ceramic ware to safeguard the surface and improve their durability. However, over-glazed decorated ceramic wares can release a toxic metal into food substances and constitute health hazards (Omolaoye et al. 2010). Also, when these glazes are improperly formulated or fired, trace amounts of heavy metals can be released through leaching into food substances in contact with the defective enamel surface (Lehman 2002). Furthermore, when colored glazes are used, basic compounds of lead, cadmium, chromium, zinc, and other heavy metals are present. They present a potential health hazard to ceramic pottery makers and consumers, since they can be leached from the glaze when used with acidic foods or alkaline foods (Belgaied 2003). This tendency towards leaching ability depends on several factors, including glaze composition, firing conditions, pH, temperature, and physical properties of food and duration of contact.

Silica is the fundamental glaze material, it occurs in nature as quartz, and it is used to facilitate the fusion of clay and the glaze material in ceramic production. Due to the relatively high melting temperature of silica, flux is added to lower the melting point. Lead is commonly used as a flux because it possesses the ability to melt at low temperature and imparts other functionally valuable and esthetic qualities to ceramics. Oxides of lead, cadmium, potassium, aluminum, zinc, nickel, copper, iron, cobalt, silicon, chromium, manganese, and arsenic are commonly used in glazes with lead oxide (PbO), making the major component of ceramic materials to be 24–32% (by weight) in lead crystal glass up to 50% in glazes and up to 80% in enamels (Nordyke 1984). Cadmium oxide (CdO) when combined with Se and other elements produces bright yellow, orange, and red colors, depending on the combination, and may be present up to 7% in glazes and decorations (Nordyke 1984; Hight 2001).

Heavy metals have been considered as a major risk to humans because of their acute and chronic toxicity, and many steps have been taken to reduce or prevent their ingestion. Heavy metal toxicity can result in damaged or reduced mental and central nervous function and lower energy levels and can cause damage to the blood composition, lungs, kidney, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that resemble Parkinson's disease, muscular dystrophy, and multiple sclerosis (Khan et al. 2011). In many countries, national legislation and international standards have been used by the authorities to monitor and regulate the possible release of lead and cadmium from all the potential sources (ASTM 2006). The European Union decided to monitor the foodwares for lead and cadmium leaching and set a Directive 84/500/EC which had a standard limit of 4.0 and 0.3 mg L^{-1} for the migration of lead and cadmium, respectively, from ceramic wares used for food (Demont et al. 2012).

This study, therefore, focused on the determination and assessment of the concentration of heavy metals and the leaching levels of the metals in some commonly used ceramic foodwares in Nigeria.

Materials and methods

Reagents used and sterilization of apparatus

All glasswares, polypropylene beakers, Teflon beakers, and polyethylene sample bottles used were first washed with liquid detergent, rinsed with distilled water, and then soaked in 10% nitric acid (HNO_3; *v*/*v*) for 48 h. They were then rinsed thoroughly with double-distilled water. Thereafter, the non-volumetric wares were oven dried for 12 h at a temperature of 80 °C. All reagents used [HNO_3 (Riedel-de-Haën, Germany), hydrofluoric acid (HF; Sigma-Aldrich Chemical, Germany), and acetic acid (CH_3COOH; British Drug House (BDH) Chemical Limited, Poole, England) were of analytical or higher grade. All the metal reference standards used are ISO 17025 certified and obtained from MRS Scientific Ltd., Wickford, Essex, UK.

Sample collection and pretreatment

Sixteen ceramic foodware samples including five plates, six mugs, three saucers, and two jugs, made by various manufacturers and imported from various countries, were purchased randomly from open markets in Lagos State and Ile-Ife, Osun State, Southwest Nigeria. The samples were of different colors and configurations and were coded A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, and P as shown in Table 1. The ceramic samples were washed, rinsed with distilled water, and subsequently dried at room temperature prior to analysis.

Leaching test

Samples were subjected to acid leaching test to investigate the release of heavy metals. Leaching tests were done following ASTM C738-94 (2006) using 4% acetic acid as the test simulant. Accurately measured 250 mL of 4% acetic acid solution was poured into each of the ceramic foodwares and covered with aluminum foil. Samples were left undisturbed for 24 h at room temperature. Thereafter, the testing solutions

Table 1 Description of ceramic foodwares

Sample code	Type of ceramic foodware	Color of ceramic foodware
A	Mug	White
B	Saucer	White
C	Jug	Navy blue
D	Mug	White and yellow
E	Plate	White and blue pattern with orange floral
F	Plate	White
G	Saucer	Cream and brown
H	Plate	White and brown
I	Mug	Red
J	Plate	White with green and red floral
K	Jug	Black
L	Saucer	White with blue floral
M	Plate	Dark brown and yellow
N	Mug	Black
O	Mug	Light brown and white
P	Mug	Dark brown and white

were taken for metal analysis using an atomic absorption spectrophotometer.

Acid digestion of samples for total metal determination

For each sample, the entire ceramic item including the glaze, decoration, and ceramic base material was ground to fine powder in a Rocklabs pulverizer. Acetone was used to clean the sample compartment in the pulverizer after each sample was pulverized to ensure no cross contamination occurred. Pulverized samples were then sieved with a 325-μm sieve and digested with acids for total metal concentrations. To achieve this, accurately weighed 0.25 g of ceramic powder was digested in Teflon beakers with 9 mL of nitric acid and 3 mL of hydrofluoric acid (HNO_3/HF; 3:1) on a thermostated hot plate between 180 and 220 °C in a fume hood. The content of the Teflon beaker was replenished with more HNO_3 and HF in a ratio of 3:1 to avoid total evaporation until all solid has been dissolved. When the content of the Teflon beaker had been reduced to about 0.5 mL, distilled water was added and allowed to boil. It was then removed from the hot plate and allowed to cool to room temperature before it was quantitatively filtered and made up to the mark in a 50-mL volumetric flask. Flame atomic absorption spectrometry (FAAS) (AA990F; PG Instrument Ltd., UK) was used to quantify the heavy metal concentrations in the digested samples. Self-reversal background correction was employed, and hydride unit was used for determination of arsenic. Air and acetylene were used, and the wavelengths (nm) for the metal determination are as follows: As (193.8), Pb (283.3), Cd (228.8), Cu (324.8), Cr (357.9), Zn (213.8), Mn (279.5), and Fe (248.3).

Determination of metal oxides in the ceramic samples

One gram of the ground powder of each ceramic sample was pelletized and analyzed to quantify the amount of their metal oxide content using particle-induced X-ray emission spectroscopy (PIXES). The PIXES experiments were performed using a 3.0 MeV proton beam from a 1.7 MV Tandem Pelletron Accelerator, model 5SDH, built by the National Electrostatics Corporation (NEC), USA, available at the Center for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria. The instrument is equipped with a radiofrequency (RF) charge exchange ion source furnished to provide proton and helium ions. It is equipped with a general purpose scattering chamber designed to carry out Rutherford backscattering spectrometry (RBS), proton-induced gamma-ray emission (PIGE), elastic recoil detection analysis (ERDA), and a special arrangement for particle-induced X-ray emission (PIXE) studies. The vacuum obtained inside the experimental chamber was of the order of 10–7 Torr. The technical parameters of the 5SDH Tandem Pelletron Accelerator include terminal voltage of 0.3–1.7 MV, proton (H^+) beam energy of 0.6–3.4 MeV, $4He^+$ beam energy of 0.6–3.4 MeV, $4He^{2+}$ beam energy of 0.9–5.1 MeV, proton beam current of 100–200 nA, $4He^+$ beam current of 200–500 nA, and variable beam spot sizes of 1, 2, 4, and 8 mm.

Quality assurance

Blank determinations were done to ascertain the background levels of the metals analyzed in the reagents used for the leaching and total metal content procedures. Recovery analyses were carried out to establish the efficacy of the analytical procedure for the total metal analysis. Samples were fortified with the standard solution of the metal analytes at the concentration of 1000 μg g^{-1}. An aliquot of the fortified sample was digested as described earlier and analyzed using atomic absorption spectrometry (AAS). Triplicate analyses were done to establish the reproducibility of the results obtained in this study. Kaolin reference standard (STD-SA69) was analyzed for the PIXE analysis to ensure the accuracy of the experimental procedure.

Results and discussion

Quality control and validation of the analytical technique

The reliability of the analytical procedures adopted in this study was tested in terms of sensitivity, precision, and accuracy. External calibration was used for the quantification of the levels of the heavy metals analyzed in the samples. The linear correlation coefficient (R^2) obtained for the calibration curve of each heavy metal determined was ≥0.996. Results from the blanks were subtracted from those of the samples to account for the background contributions. The results of recovery of heavy metals from spiked samples (Table 2) ranged from 77.08% for arsenic to 107.21% for lead with a percentage relative standard deviation (%RSD) of <10%. The recovery results were adjudged acceptable and confirmed the efficiency of the analytical procedure used in this study.

As shown in Table 3, the concentration obtained for each element determined in the Kaolin standard agreed well with the certified values. This established the accuracy and efficiency of the PIXE technique.

Total metal content

The results showing the mean concentrations of Pb, Cd, Zn, As, Cu, Cr, Mn, and Fe analyzed in the ceramic samples are presented in Table 4. The results showed concentrations in the following ranges: 26.45–2071.46, 5.20–547.00, 1.24–2681.02, 2590.00–8848.40, 6.42–654.66, 112.69–649.95, 63.38–2518.51, and 3786.51–8249.44 μg g^{-1} for Pb, Cd, Zn, As, Cu, Cr, Mn, and Fe, respectively. The concentrations of As, Fe, and Mn were higher than those of other metals analyzed with Cd showing the least concentration in the samples.

The concentrations of Pb and Cd were found to be surprisingly high in samples A, D, G, I, M, and N with sample I having the highest levels. These samples have very shiny appearance, and this may be due to the added lead oxide in their glazes. The red and yellow colorations in samples D, I, and M may be due to cadmium and selenium coloration in their glazes (Nordyke 1984; Hight 2001), thereby yielding high levels of cadmium. Lead produces physiological and neurological effects in humans, and severe lead poisoning can lead to coma and death. Lead is also very toxic to fetus, infants, and young children, while Cd is known to have acute and chronic effects, such as gastrointestinal disorders, cancer, and kidney problems (Sheets 1998). It is, therefore, important to exercise caution when using ceramic foodwares. The highest concentration of chromium was in sample N which may be associated to its black coloration. Chromium oxide has been used to obtain black and green shades in glazes; hence, its detection in sample N is expected which would have had a high chromium content most likely due to the added chromium oxide to obtain its black-colored glaze (Britt 2007). In the presence of zinc, chromium can produce brown colorations as indicated in samples H, O, and P with their high zinc and chromium content. Iron was detected in all the samples, and the highest level was observed in sample C. Samples O and P also showed high concentrations of iron which may not be unconnected with their brown colorations.

Table 2 Percent total metal recovery from spiked samples ($n = 3$)

Elements	Concentration spiked (μg g^{-1})	Concentration recovered (μg g^{-1}) ± SD	% recovery ± RSD
Pb	1000	1072.19 ± 38.75	107.21 ± 3.57
Cd	1000	897.11 ± 18.69	89.71 ± 2.09
Zn	1000	990.40 ± 14.74	99.04 ± 2.56
Cu	1000	1069.31 ± 15.71	106.93 ± 2.46
As	1000	770.82 ± 11.56	77.08 ± 1.75
Fe	1000	970.43 ± 9.39	97.04 ± 2.59

Arsenic was detected in all the samples studied at relatively high levels when compared to the other metals analyzed. Arsenic trioxide has been known to be used in ceramics' production as an opacifying oxide. Arsenic trioxide is considered to be over four times as toxic as lead oxide. Therefore, there is a very high human health risk associated with using ceramics containing a high concentration of As (Perez-Arantegui et al. 2004; Chappell et al. 2003; Mass 1992). It has been established that over 137 million people suffer from arsenic-related problems each year (WHO 2001). Continued exposure to a high concentration of arsenic, therefore, may produce acute toxic effects on humans, which can be quickly diagnosed; however, chronic exposure to low doses of arsenic may give rise to cancer (Hayes 1997; Roy and Saha 2002; IARC 2009).

Table 3 Concentration of metals in the Kaolin standard analyzed with PIXE and the certified value for the metals

Element	Concentration obtained (μg g^{-1})	Certified value	Oxides	Oxide value (%)
Na	5662.40	5680	NaO	0.76
Mg	11,188.40	11,160	MgO	1.86
Al	76,702.60	76,700	Al_2O_3	14.49
Si	311,526.80	311,300	SiO_2	66.65
P	1220.40	1222	P_2O_5	0.28
K	16,327.40	16,300	K_2O	1.97
Ca	17,142.70	16,900	CaO	2.40
Ti	4644.90	4660	TiO_2	0.08
V	244.20	240	V_2O_5	0.04
Cu	49.60	46	CuO	0.0162
Cr	223.90	223	Cr_2O_3	0.03
Mn	1205.80	999	MnO	0.16
Fe	5239.00	5200	Fe_2O_3	0.75
Zn	69.20	68	ZnO	0.01
Rb	64.70	63	RbO	0.01
Sr	106.90	104	SrO	0.01
Zr	268.60	270	ZrO_2	0.04

Table 4 Total metal concentrations in the ceramic samples using an atomic absorption spectrophotometer (μg g^{-1}) (mean ± SD) ($n = 3$)

Samples	Metals							
	Pb	Cd	Zn	As	Cu	Cr	Mn	Fe
A	206.89 ± 3.03	<2.8[a]	16.82 ± 0.37	8649.90 ± 99.40	292.69 ± 6.42	283.23 ± 10.50	643.91 ± 17.72	4804.79 ± 65.5
B	<1.3[a]	5.20 ± 0.02	<3.3[a]	4503.50 ± 57.10	342.48 ± 27.25	226.11 ± 17.32	85.89 ± 2.15	5225.67 ± 80.9
C	<1.3[a]	47.32 ± 0.99	1.24 ± 0.03	2590.00 ± 48.00	<4.5[a]	346.10 ± 13.91	1378.13 ± 44.4	8249.44 ± 95.1
D	<1.3[a]	120.48 ± 1.57	564.87 ± 8.11	8490.90 ± 92.40	<4.5[a]	369.89 ± 27.78	96.14 ± 3.91	6719.83 ± 63.3
E	55.61 ± 1.83	<2.8[a]	2650.02 ± 45.3	8848.40 ± 68.70	282.46 ± 8.34	134.89 ± 7.41	370.74 ± 17.13	6459.02 ± 54.9
F	<1.3[a]	<2.8[a]	2284.39 ± 39.4	7938.20 ± 73.70	<4.5[a]	235.31 ± 10.98	88.09 ± 3.29	5770.60 ± 50.1
G	145.11 ± 6.85	40.72 ± 1.03	334.44 ± 9.21	5379.01 ± 61.10	343.88 ± 21.04	353.88 ± 5.52	248.34 ± 21.03	4208.19 ± 52.4
H	<1.3[a]	86.39 ± 2.01	173.42 ± 9.21	6591.54 ± 83.20	<4.5[a]	313.74 ± 5.52	133.15 ± 7.70	6136.05 ± 75.50
I	2071.46 ± 48.90	547.09 ± 15.72	2130.55 ± 59.10	6686.80 ± 69.70	248.41 ± 16.43	248.29 ± 16.64	175.57 ± 7.68	6332.13 ± 65.20
J	<1.3[a]	<2.8[a]	<3.3[a]	7669.56 ± 72.30	6.42 ± 0.04	112.69 ± 8.95	126.95 ± 2.76	5267.20 ± 40.30
K	122.88 ± 48.40	<2.8[a]	1104.45 ± 45.60	5536.61 ± 76.80	148.54 ± 0.83	144.72 ± 4.99	238.72 ± 15.79	7585.44 ± 54.70
L	26.45 ± 0.44	<2.8[a]	5.52 ± 0.24	8441.56 ± 85.90	62.75 ± 1.76	<5.4[a]	63.38 ± 1.67	4730.08 ± 47.50
M	<1.3[a]	376.86 ± 7.03	<3.3[a]	6237.22 ± 78.50	64.69 ± 3.01	266.36 ± 5.31	95.67 ± 3.52	3786.51 ± 59.70
N	133.40 ± 3.06	95.95 ± 3.58	194.77 ± 4.93	2912.03 ± 54.50	<4.5[a]	649.95 ± 17.17	2518.51 ± 79.20	7195.86 ± 80.40
O	<1.3[a]	<2.8[a]	2681.95 ± 40.70	6612.26 ± 68.20	654.66 ± 22.85	324.72 ± 9.12	277.38 ± 18.57	7675.13 ± 88.40
P	<1.3[a]	<2.8[a]	979.67 ± 15.97	6319.73 ± 84.70	36.06 ± 1.58	292.26 ± 6.71	533.30 ± 28.35	7730.30 ± 84.30

[a] Shows the detection limit in micrograms per gram

High correlation coefficients were obtained between Pb/Cd and Cr/Mn, which implies that the presence of these elements in the samples was dependent on each other. Moderate correlation coefficients for Zn/Cu and Mn/Fe suggest that each paired metal was associated with one another in the samples. The negative correlation coefficients for Pb/Mn and Cu/Cr suggested that the presence of one of these metals can substitute the other in the sample, and as the concentration of one of these paired metals increases in the sample, the other decreases and vice versa. Analysis of variance (ANOVA) showed significant variations at $P < 0.05$ between ceramic samples in their total metal determined. The concentrations of lead in samples A and E are significantly different; however, there was no significant difference between the concentrations in samples G, K, and N. In the determination of cadmium, samples M and N showed a significant difference. For chromium levels, samples A, B, F, I, M, and P showed no significant difference.

Levels of metal oxides in the ceramic samples

Table 5 showed the levels of the metal oxides determined in the ceramic samples using PIXE. The results indicated that the ceramic samples contained different metals and their oxides in varied concentrations. Elements such as sodium, magnesium, aluminum, silicon, phosphorus, potassium, calcium, titanium, vanadium, chromium, manganese, iron, copper, zinc, rubidium, strontium, zirconium, barium, lead, and their oxides were determined and obtained at various levels in the samples. Oxides of Si and Al had the highest concentrations followed by the oxides of Na, K, Ca, and Fe with concentrations ranging from 23.04% in sample A to 47.76% in sample M for Al_2O_3, from 44.68% in sample H to 65.45% in sample A for SiO_2, from 1.56% in sample F to 12.55% in sample K for Na_2O, from 1.41% in sample K to 3.11% in sample A for K_2O, from 0.42% in sample A to 1.97% in sample C for Fe_2O_3, and from 0.25% in sample A to 1.79% in sample J for CaO. The high concentrations of the oxides of Si, Al, Na, P, and K may be due to the basic ingredients used in the production of ceramics. While SiO_2 provides the main body for the glaze, Al_2O_3 enhances the viscosity of the glaze by cross-linking the silica networks, and then the fluxes are generally alkali or alkaline earth metal oxides and are intended to lower the melting point of the mixture to the temperature of firing (Rhodes 1973).

A comparison of the total metal concentrations using AAS (Table 4) and the oxides of the metals determined by PIXE (Table 5) shows that the variation of the total metal concentrations follow the same trend with the metal oxides; the metal oxide concentration increases as the concentration of the total metal increases and vice versa.

Table 5 Levels of metal oxides in the ceramic samples determined with PIXE

Metal oxides	Sample identity and concentrations (%)															
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Na_2O	2.33	3.26	0.00	10.98	0.00	1.56	3.25	0.00	6.67	3.01	12.53	2.22	1.61	1.96	1.64	7.67
MgO	1.09	0.78	0.87	0.66	0.46	1.15	0.77	0.56	1.07	0.61	2.56	1.12	0.73	0.57	0.53	0.34
Al_2O_3	23.04	26.49	27.34	29.77	33.49	43.29	32.22	41.80	42.70	46.80	44.97	46.88	47.76	42.12	42.63	30.11
SiO_2	65.45	63.32	57.58	52.50	47.04	45.77	46.14	44.68	53.65	47.79	64.04	56.11	52.32	51.36	52.95	51.53
P_2O_5	0.35	0.30	0.40	0.28	0.29	0.24	0.00	0.00	0.49	0.00	0.55	0.24	0.28	0.00	0.11	0.13
K_2O	3.11	1.52	2.10	1.78	2.37	2.01	2.13	1.78	1.89	2.30	1.41	3.02	2.66	2.54	2.52	1.93
CaO	0.25	0.66	0.74	1.29	0.99	1.14	0.82	1.03	0.89	1.79	0.93	1.45	1.51	1.42	1.63	0.82
TiO_2	0.03	0.27	0.55	0.29	0.38	1.01	0.30	0.88	0.64	0.83	0.20	0.73	0.93	0.79	0.52	0.21
Cr_2O_3	0.03	0.03	0.04	0.04	0.07	0.04	0.03	0.14	0.03	0.09	0.02	0.04	0.05	0.03	0.05	0.05
MnO	0.05	0.01	0.13	0.04	0.06	0.01	0.04	0.01	0.02	0.01	0.02	0.01	0.01	0.36	0.04	0.06
Fe_2O_3	0.42	0.49	1.97	1.38	1.25	0.95	0.78	0.74	1.07	0.99	1.17	0.92	0.78	1.23	1.05	1.08
As_2O_3	0.03	0.00	0.00	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01
CuO	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.01
ZnO	0.01	0.00	0.01	0.26	0.26	0.08	0.04	0.22	0.16	0.00	0.08	0.04	0.00	0.00	0.26	0.08
Rb_2O	0.05	0.00	0.00	0.02	0.03	0.00	0.01	0.01	0.02	0.00	0.01	0.06	0.01	0.00	0.01	0.01
PbO	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.00	0.01	0.00	0.00	0.00	0.00	0.00
SrO	0.00	0.02	0.00	0.00	0.00	0.02	0.03	0.08	0.03	0.00	0.00	0.00	0.02	0.02	0.00	0.00
V_2O_5	0.00	0.03	0.00	0.02	0.02	0.04		0.03	0.02	0.03	0.00	0.00	0.03	0.05	0.02	0.01
ZrO_2	0.00	0.00	0.10	0.33	0.40	0.41	0.02	0.00	0.35	0.04	0.67	0.00	0.24	0.05	0.26	0.00
BaO	0.00	0.00	0.00	0.72	0.00	0.00	0.00	0.00	0.84	0.00	0.33	0.00	0.43	0.00	0.00	0.49

The concentration is expressed in percentages (%)

Barium and its oxide were detected in samples D, I, K, M, and P at concentrations ranging from 0.33% in sample K to 0.84% in sample I. Barium acts as a strong flux and, when combined with lead, can give a smooth matte finish to ceramics at low firing (Hopper 2006). It is likely that barium has been used to replace lead in frit formulations for glazes due to the known toxicity of lead. The soluble form of barium compounds like barium carbonate is toxic and can cause vomiting, gastrointestinal problems, and paralysis. Though the toxic limit of barium leading to health hazards in human is not well known (Assimon et al. 1997), it is important to limit our exposure to such materials that are capable of posing potential dangers to human health.

Iron and its oxide were relatively high in all the samples. Red iron oxide (Fe_2O_3) is commonly used to produce earthy red and brown colorations. Iron is a tricky colorant because of its ability to yield different colors under different circumstances, hence its high content in many ceramic wares. At low percentages (0.5–2%) and in the presence of potassium, it will become light blue or light blue green in reduction. When used in combination with calcium, red iron oxide can become pale yellow or amber on oxidation or green on reduction. Common percentages for red iron range from 1 up to 10% in ceramics (Rhodes and Hopper 2000). Manganese oxide is typically a high temperature fluxing oxide but can be used at lower temperatures as an opacifier; potassium and sodium are powerful fluxes at any temperature. Strontium oxide is usually used as a flux at high temperatures but can be used in small quantities at low temperatures to a good effect; it is often used as a replacement for barium in glazes in order to reduce toxicity (Williams 2006). Zirconium oxide and titanium oxide generally produce opaque qualities in the glaze regardless of the firing temperature.

The results of the correlation analysis showed a high correlation for Na_2O/MgO, Na_2O/SiO_2, MgO/SiO_2, MgO/P_2O_5, MgO/ZrO_2, SiO_2/P_2O_5, P_2O_5/ZrO_2, K_2O/CaO, CuO/TiO_2, V_2O_5/MnO, and PbO/BaO at 0.73, 0.69, 0.93, 0.78, 0.82, 0.77, 0.80, 0.72, 0.72, 0.75, and 0.72, respectively. This suggests a strong positive linear relationship between each of the paired oxide, in the ceramic samples, and their presence is dependent on (or associated with) one another. Also, high negative correlations were recorded for Na_2O_3/K_2O (−0.92), Na_2O/CaO (−0.81), SiO_2/Cr_2O_3 (−0.71), and CaO/BaO (−0.76), indicating a strong negative linear relationship between the paired oxides. The presence of one of these paired oxides can substitute for the other in the ceramic samples, and as the concentration of one of these paired oxides increases in the ceramic samples, the other decreases and vice versa.

Leached metals

The results of concentrations of heavy metals that were leached from the ceramic foodwares when tested with 4% acetic acid in order to assess the level of safety or exposure risk that the ceramics pose to the end users are presented in Table 6. The results gave an indication of the possibility of relationship between the glaze coloration in the samples and their leaching potential. As seen in Table 6, metals migrated from the ceramic samples exposed to the leaching conditions gave concentrations in the ranges 0.109–0.967, 0.012–0.276, 0.002–4.191, 1.927–15.001, 0.009–0.407, 0.092–0.603, 0.007–2.143, and 0.009–11.529 mg L^{-1} for Pb, Cd, Zn, As, Cu, Cr, Mn, and Fe, respectively, where they were detected above the instrument detection limits. The amount of lead leached into the testing solution is highest in sample I while sample E had the lowest concentration. The highest concentration of cadmium was also observed in sample I (0.276 mg L^{-1}). The high concentration of cadmium in sample I may be attributed to its red-colored glaze. Cadmium has been used with selenium in ceramic glazes to give bright red and yellow colorations (Belgaied 2003). In none of the samples were the released levels of lead and cadmium exceeded the standard limits (4 mg L^{-1} for lead and 0.3 mg L^{-1} for cadmium) according to the European Council Directive and USFDA for ceramic articles, although sample I almost reached the permissible limit for cadmium.

High levels of chromium and manganese were observed to leach from sample N. This may be due to its black coloration which can be attributed to chromium use in glazes to give black colorations (Britt 2007). Arsenic was observed to leach from all the samples. Arsenic leaching has been reported from poorly glazed and non-glazed potteries using 4% acetic acid solution (Henden et al. 2011). Inorganic arsenic is a human poison, whereas organic arsenic is less harmful. The long-term effects of consuming water with an arsenic concentration of 17 μg mL^{-1} have been shown to have significant health effects (Kosnett 2005). Colorants used in glazes contain the same kind of pigments used in ordinary oil and water colors; hence, they contain basic compounds of lead, chromium, zinc, and copper. Samples were found to be safe with metal leaching; however, ceramic wares observed to be safe from metals like lead may leach in high amounts once it is worn down by long-term usage (Mohamed et al. 1995), as leaching is a function of time.

The results obtained from the leaching studies were analyzed statistically. Correlation matrix was used to examine the interrelationship between the metals in the samples. High correlation coefficients for Pb/Cd, Zn/Fe, and Cr/Fe were obtained which suggest the relationship between them and their presence in the leachate is dependent on each other. However, low correlation coefficients were found for Pb/As, Zn/Mn, and As/Cu. This indicated no significant relationship with each other. The negative correlation coefficients between Pb/Cu, Cd/Zn, and As/Cr indicated that there was a competition or blockage between the paired metals in the leaching solution. ANOVA results showed that at $P < 0.05$ significant level, there were variations in the metals leached from the samples.

Table 7 shows the leached metal concentrations in relation to their total metal concentrations in each of the samples analyzed. From the figure, the concentration of some metals leached from the samples (i.e., samples A, D, I, M, and N) was in line with their total metal levels; however, there were some inconsistencies observed in samples E, F, H, and L. Belgaied (2003) reported that heavy metals leaching in a ceramic ware are in relation to various factors such as glaze composition, firing condition, pH, temperature, physical properties of food, and duration of exposure of these ceramic glazes to food. Improperly formulated or fired glazes can release toxic amounts of heavy metals via leaching into food substances (Omolaoye et al. 2010). Glazes that do not have the proper balance of fluxes, silica, and alumina may not mature well and fuse properly to the ceramic body. Samples E, F, H, and K may have inaccurately combined glaze compositions or improperly fired glazes in their silicate matrix such that these metals are easily extracted irrespective of their total metal content. The extraction of these metals from ceramic wares increases with temperature, which could be the result of lower diffusion activation energy and high diffusion coefficient caused by high temperature that makes the ion exchange reactions occur more rapidly, and hence, the extraction of these metals occurs more easily (Dong et al. 2013). Lead released decreases linearly with the increase of pH value under a certain temperature.

Ratio of leached metals with their oxide compositions

On the average, the percentage ratios of the metal oxides determined in the samples gave the values of 0.39, 1.27, 6.79, 0.38, 4.11, 5.62, 81.91, and 0.00% for PbO, As_2O_3, ZnO, CuO, Cr_2O_3, MnO, Fe_2O_3, and CdO, respectively, while the percentage ratio values obtained for the leached metals from the ceramics were 0.8, 83, 3, 3, 1, 8, 12, and 1% for Pb, As, Zn, Cu, Cr, Mn, Fe, and Cd, respectively. Comparing the ratio of the metals leached from the ceramic wares with the ratio of the metal oxides in the ceramics, it is obvious that not all the metals detected in the ceramic samples were domiciled in the glaze, but in the clay material used for the ceramic, and were not available to leach into foods. The more susceptible of the metals to leaching are those present in the ceramic as the glaze components and

Table 6 Leached metal concentrations (mg L^{-1}) in the ceramic samples (mean ± SD) (n = 3)

Samples	Metals							
	Pb	Cd	Zn	As	Cu	Cr	Mn	Fe
A	0.247 ± 0.004	<2.8[a]	<3.3[a]	15.001 ± 0.012	0.241 ± 0.001	0.240 ± 0.001	0.007 ± 0.001	<4.3[a]
B	<1.3[a]	<2.8[a]	<3.3[a]	5.054 ± 0.005	0.154 ± 0.002	<5.4[a]	<2.2[a]	<4.3[a]
C	<1.3[a]	0.012 ± 0.001	<3.3[a]	<1.2[a]	<4.5[a]	<5.4[a]	0.083 ± 0.002	0.009 ± 0.001
D	<1.3[a]	0.112 ± 0.001	0.039 ± 0.001	6.778 ± 0.003	<4.5[a]	<5.4[a]	0.310 ± 0.001	0.184 ± 0.001
E	0.109 ± 0.002	<2.8[a]	0.318 ± 0.001	10.567 ± 0.009	0.307 ± 0.002	<5.4[a]	0.239 ± 0.002	0.326 ± 0.002
F	<1.3[a]	<2.8[a]	<3.3[a]	2.894 ± 0.001	<4.5[a]	<5.4[a]	<2.2[a]	<4.3[a]
G	<1.3[a]	0.014 ± 0.001	<3.3[a]	4.401 ± 0.003	0.407 ± 0.002	<5.4[a]	0.017 ± 0.001	<4.3[a]
H	<1.3[a]	0.087 ± 0.003	<3.3[a]	5.806 ± 0.005	<4.5[a]	<5.4[a]	0.108 ± 0.001	<4.3[a]
I	0.967 ± 0.011	0.276 ± 0.005	<3.3[a]	6.871 ± 0.009	<4.5[a]	<5.4[a]	0.067 ± 0.001	<4.3[a]
J	<1.3[a]	<2.8[a]	<3.3[a]	4.555 ± 0.002	<4.5[a]	<5.4[a]	0.061 ± 0.001	<4.3[a]
K	<1.3[a]	<2.8[a]	0.385 ± 0.001	2.118 ± 0.003	0.324 ± 0.003	<5.4[a]	0.087 ± 0.002	<4.3[a]
L	<1.3[a]	<2.8[a]	0.002 ± 0.000	1.927 ± 0.003	<4.5[a]	<5.4[a]	<2.2[a]	0.139 ± 0.002
M	<1.3[a]	0.097 ± 0.001	<3.3[a]	2.463 ± 0.000	0.009 ± 0.001	0.166 ± 0.002	0.068 ± 0.000	<4.3[a]
N	<1.3[a]	0.062 ± 0.003	0.032 ± 0.002	<1.2[a]	<4.5[a]	0.603 ± 0.001	2.143 ± 0.001	6.261 ± 0.001
O	<1.3[a]	<2.8[a]	4.191 ± 0.015	3.423 ± 0.003	0.361 ± 0.002	0.597 ± 0.002	0.616 ± 0.002	11.529 ± 0.001
P	<1.3[a]	<2.8[a]	0.828 ± 0.002	5.049 ± 0.004	<4.5[a]	0.092 ± 0.001	0.422 ± 0.001	6.598 ± 0.003
Permissible limit (mg L^{-1})	4.0	0.3	–	–	–	–	–	–

[a] Detection limit of metal in micrograms per liter

Table 7 Relationship between leaching metal concentration (mg L^{-1}) and total metal concentration (μg g^{-1}) in the ceramic samples

Samples	Pb		Cd		Zn		As		Cu		Cr		Mn		Fe	
	LM	TM	LM	TM	LM	TM	LM	TM	LM	TM	LM	TM	LM	TM	LM	TM
A	0.247	206.89	BDL	BDL	BDL	16.82	15.001	8649.90	0.241	292.69	0.240	283.23	0.007	643.91	BDL	4804.79
B	BDL	BDL	BDL	5.20	BDL	BDL	5.054	4503.50	0.154	342.48	BDL	226.11	BDL	85.89	BDL	5225.67
C	BDL	BDL	0.012	47.32	BDL	1.24	BDL	2590.00	BDL	BDL	BDL	346.10	0.083	1378.13	0.009	8249.44
D	BDL	BDL	0.112	120.48	0.039	564.87	6.778	8490.90	BDL	BDL	BDL	369.89	0.310	96.14	0.184	6719.83
E	0.109	55.61	BDL	BDL	0.318	2650.02	10.567	8848.40	0.307	282.46	BDL	134.89	0.239	370.74	0.326	6459.02
F	BDL	BDL	BDL	BDL	BDL	2284.39	2.894	7938.20	BDL	BDL	BDL	235.31	BDL	88.09	BDL	5770.60
G	BDL	145.11	0.014	40.72	BDL	334.44	4.401	5379.01	0.407	343.88	BDL	353.88	0.017	248.34	BDL	4208.19
H	BDL	BDL	0.087	86.39	BDL	173.42	5.806	6591.54	BDL	BDL	BDL	313.74	0.108	133.15	BDL	6136.05
I	0.967	2071.46	0.276	547.09	BDL	2130.55	6.871	6686.80	BDL	248.41	BDL	248.29	0.067	175.57	BDL	6332.13
J	BDL	BDL	BDL	BDL	BDL	BDL	4.555	7669.56	BDL	6.42	BDL	112.69	0.061	126.95	BDL	5267.20
K	BDL	122.88	BDL	BDL	0.385	1104.45	2.118	5536.61	0.324	148.54	BDL	144.72	0.087	238.72	BDL	7585.44
L	BDL	26.45	BDL	BDL	0.002	5.52	1.927	8441.56	BDL	62.75	BDL	BDL	BDL	63.38	0.139	4730.08
M	BDL	BDL	0.097	376.86	BDL	BDL	2.463	6237.22	0.009	64.69	0.166	266.36	0.068	95.67	BDL	3786.51
N	BDL	133.40	0.062	95.95	0.032	194.77	BDL	2912.03	BDL	BDL	0.603	649.95	2.143	2518.51	6.261	7195.86
O	BDL	BDL	BDL	BDL	4.191	2681.95	3.423	6612.26	0.361	654.66	0.597	324.72	0.616	277.38	11.529	7675.13
P	BDL	BDL	BDL	BDL	0.828	979.67	5.049	6319.73	BDL	36.06	0.092	292.26	0.422	533.30	6.598	7730.35

LM leached metal concentration in the sample (mg L^{-1}), *TM* total metal concentration in the sample (μg g^{-1}), *BDL* below detection limit

Table 8 Ratio of leached metals with their percentage oxide compositions

Sample	Leached ratio (%)								Oxide ratio (%)						
	Pb/	As/	Zn/	Cu/	Cr/	Mn/	Fe/	Cd	Pb/	As/	Zn/	Cu/	Cr/	Mn/	Fe
A	1.00:	95.0:	0.00:	1.00:	1.00:	0.40:	0.00:	0.00	1.52:	4.51:	1.70:	1.03:	4.52:	9.41:	77.11
B	0.00:	97.0:	0.00:	3.00:	0.00:	0.00:	0.00:	0.00	0.00:	0.52:	0.00:	1.23:	5.72:	1.91:	90.72
C	0.00:	0.00:	0.00:	0.00:	0.00:	79.0:	8.00:	11.0	0.00:	0.00:	0.45:	0.00:	1.83:	6.07:	91.61
D	0.00:	90.0:	0.50:	0.00:	0.00:	4.00:	2.00:	1.00	0.00:	1.36:	14.52:	0.24:	2.49:	2.03:	77.18
E	1.00:	89.0:	2.00:	2.00:	0.00:	2.00:	3.00:	0.00:	0.14:	1.18:	15.54:	0.32:	4.19:	3.66:	74.94
F	0.00:	99.8:	0.00:	0.00:	0.00:	0.00:	0.00:	0.00	0.00:	1.71:	6.88:	0.00:	3.66:	13.51:	86.38
G	0.00:	91.0:	0.00:	8.00:	0.00:	0.30:	0.00:	0.20	0.58:	1.03:	4.14:	1.19:	3.19:	4.25:	85.61
H	0.00:	96.0:	0.00:	0.00:	0.00:	2.00:	0.00:	1.00	0.00:	1.43:	19.39:	0.11:	12.19:	0.96:	65.89
I	12.0:	84.0:	0.00:	0.00:	0.00:	1.00:	0.00:	3.00	3.31:	0.93:	11.88:	0.37:	1.90:	1.30:	80.29
J	0.00:	98.0:	0.00:	0.00:	0.00:	1.00:	0.00:	0.00	0.00:	1.71:	0.00:	0.00:	7.99:	0.73:	89.51
K	0.00:	73.0:	13.0:	11.0:	0.00:	3.00:	0.00:	0.00	0.26:	0.71:	5.09:	0.00:	1.29:	14.51:	78.09
L	0.00:	93.0:	0.10:	0.00:	0.00:	0.00:	7.00:	0.00	0.11:	1.94:	4.11:	0.00:	3.59:	0.92:	89.31
M	0.00:	88.0:	0.00:	0.30:	6.00:	2.00:	0.00:	3.00	0.00:	1.11:	0.00:	0.00:	5.85:	1.49:	91.54
N	0.00:	0.00:	0.30:	0.00:	6.00:	23.0:	68.0:	0.60	0.28:	0.00:	0.83:	0.00:	1.77:	22.15:	74.99
O	0.00:	16.0:	20.0:	17.0:	3.00:	3.00:	55.0:	0.00	0.00:	1.04:	18.33:	1.13:	3.57:	2.83:	73.11
P	0.00:	39.0:	6.00:	0.00:	0.70:	3.00:	51.0:	0.00	0.00:	1.13:	5.84:	0.54:	3.76:	4.33:	84.39
Average ratio	0.80:	83.0:	3.00:	3.00:	1.00:	8.00:	12.0:	1.00:	0.39:	1.27:	6.79:	0.38:	4.11:	5.62:	81.91

can leach at a rate and level that can be affected by the temperature and the pH of the food. As demonstrated in Table 8, Fe_2O_3 content had the highest ratio among the oxides in all the ceramic samples but had the least ratio of metals leached from the ceramics except in samples N, O, and P where the ratio of Fe leached were 68, 55, and 51%, respectively, as opposed to the observation of leached Fe ratio of less than 10% in others. This is an indication that the Fe_2O_3 contents of most samples were in the clay material used while for samples N, O, and P, a large proportion of the Fe was in the glaze, thereby making them available to leaching into foods. The high concentration of Fe in the glazy of these three samples may be attributed to their colorations, as combination of O and P had brown color and it has been demonstrated that Fe is used in glazy ceramics to produce brown color at various degrees. So also, N has black coloration and Fe in combination with other metals may have been used to obtain the coloration as the sample also exhibited a high leaching concentration of Mn (23%). Sample C showed much lower Mn oxide than the ratio obtained in the leachate, suggesting that Mn was likely to be part of the glaze formulation for the sample.

The ratio of As_2O_3 was among the oxides with the least ratio in all the samples after PbO and CuO. However, it gave the highest ratio of leachates in all samples except in samples C and N that show no oxide for As and no As leachate. The high ratio of As in the sample is an indication that the As content may not be in the clay material, which was not available to the leaching agent but present in the glaze used to provide a protective finish and smooth surface for the clay body and to incorporate attractive coloration (Turbett and Stephenson 1978; Belgaied 2003), thereby making As in the ceramic available for migration from the ceramic to foods. Besides, there is high tendency that As in the glazes was not properly combined with the silicate matrix, improperly formulated with the glaze composition or does not meet the firing conditions of the glaze and was thus most readily extracted regardless of its oxide values in the samples.

Conclusion

This study has demonstrated that varied concentrations of heavy metals were present in ceramic foodwares and that highly decorated and colored ceramic glazes may be potential sources of heavy metals. Higher concentrations of metals were reported in the ceramic foodwares than those found in the leached experiment. The use of raw materials containing heavy metals that are considered highly hazardous should be minimized or discouraged in ceramic foodware production because of the health hazards associated with exposure to these toxic metals. Government should put necessary regulation in place to protect the unsuspecting public from exposure to high levels of toxic metals through the use of ceramic foodwares.

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