DOI:10.7598/cst2018.1440
ISSN:2278-3458

Chemical Science Transactions
2018, **7(1),** 130-136

RESEARCH ARTICLE

Assessment of Lead, Arsenic, Cadmium and Mercury Levels in Earthenware Clay Deposits at Mankessim, in Mfantsiman District, Ghana

B. V. SAMLAFO

Department of Chemistry Education, University of Education,
Winneba, Box 25, Winneba, Ghana
vsamlafo@yahoo.com

Received 4 August 2017 / Accepted 23 August 2017

Abstract: This study assessed the suitability of Mankessim clay deposits as the raw material for earthenware products in terms of toxic metal levels such as Hg, Pb and Cd and As, which impact on human health. Atomic absorption spectrometric (AAS) technique was used to determine the levels of the toxic metals in the samples. The mean levels of Hg, Pb and Cd, were within the safe limit levels. Cadmium was however below the method's detection limit at four sites. The mean Arsenic level was generally very high; however, this level was lower than the levels reported in some geophagy clays which were eaten directly. The precision and the accuracy of the analytical method (AAS) were evaluated by the use of standard reference material IAEA-Soil-7. The values obtained for the various elements in soil-7 compared favourably well with the recommended values as Spearman's correlation coefficient was +0.94. The experimental values were within ±6% of the recommended value. The measurement precision defined by the relative standard deviation was within +5%. Arsenic was found to be generally high in the study site. Potters need to find ways of reducing arsenic levels before using the raw material for any product that comes into contact with food.

Keywords: Mankessim, Earthenware, Clay, Toxic metals, Geophagy, Pottery

Introduction

Clay is a naturally occurring aluminium silicate[1]. It is principally composed of ultra-fine grain minerals. Clays are distinguished from other fine grain soils such as silt by differences in size of mineralogy. Silt is a fine soil similar to clay, however, clay is finer. It is so fine that, it is almost impossible to identify crystals from it. The distinction between clay and silt varies by discipline. Geologists, soil scientists, sedimentologists and colloid chemists all draw their distinction based on particle size in μm which in all cases has the finest particle[2]. Geotechnical engineers distinguished between silts and clays based on plasticity[2].

All clay minerals have great affinity for water. Some swell easily and may double in thickness when wet. Most clays have the ability to absorb/adsorb ions from solution and release the ions later when conditions change[3]. When a little clay is added to water, a slurry is formed, because, the clay distributes itself evenly throughout the water. This property of clay is used in the clay industry to disperse pigment evenly throughout paint[3]. A mixture of a lot of clay and a little water results in a mud that can be shaped and dried to form a relatively rigid solid. This property is exploited by potters and the ceramic industry to produce plates, cups, bowls and pipes *etc*.,[3]. Environmental industries use both properties to produce homogeneous liners for containment of waste. There are two types of clay. Primary clay remains in the place where it was formed; it is normally white in colour and of low plasticity. However, this type of clay is relatively pure. On the other hand, secondary clay moves from the parent rock and transported mainly by erosion and water from its areas of formation. Secondary clays are of various colours and of high plasticity[4].

Environmental characteristics such as nature and distribution of inorganic contaminants, such as metals and metalloids like arsenic, iron, lead, mercury and cadmium, in clay-bearing rocks have the potential to affect the use of clay in natural and industrial applications[3].

In its natural state, clay can be easily moulded and manipulated by the hand. This property is called plasticity. When heated to between 648 to 982 ^{o}C, it matures. Firing clay to its maturing temperature makes it impermeable to water. As a result, earthenware products such as pots are used to store water, for cooking and as pepper-grinding bowls in Ghanaian homes and restaurants[5]. The variation in the mineral contents of these clays such as kaolinite, gibbsite, hydrous iron oxide, *etc*., contributes to the different colours found in the clays and their various products. Thus, colour, plasticity, absorption qualities, hardness, cohesion, fineness of grains and refractory characteristics, *etc*., are a few of the physical characteristics used to distinguish between the various clay types[4].

However, traditional potters do not perform any chemical analysis on the clay samples before; they are used in making earthenware products. If the geology of the rocks/soil from which the clay is formed is high in toxic heavy metals, then the use of these products for cooking, storage of water and grinding of pepper becomes a health hazard to people who use it.

Arsenic, mercury, lead and cadmium are referred to as toxic elements and have been linked to adverse reproductive outcomes, neurological disorders and impaired cognitive development in children[6]. For example, one study reported high levels of arsenic, lead and cadmium in geophagy clay eaten by Bangladeshi pregnant women[7]. There have also been other reports of the presence of these harmful elements in geophagy clays from other places such as Ghana and Kenya[7]. Several studies have examined a number of reproductive end-points to arsenic exposure and the results suggest foetal, neonatal and postnatal mortality, lowered birth weight, spontaneous abortion, still birth and congenital malformation. However, there is no consistent evidence for any one particular end-point[8].

Mercury alters biological system because of its affinity for sulfhydryl (-SH) groups which are functional parts of most enzymes and hormones. It induces a change in cell structure while disrupting critical electron transfer reaction leading to cells being perceived as foreign by the body's immune defence and repair system[9]. Long term exposure of Cd affects calcium metabolism and prevent deposition of Ca in bones[10].

Children may appear inattentive, hyperactive and irritable even at low levels of lead exposure. Children with greater lead levels may be affected with delayed growth, decreased intelligence, short-term memory and hearing loss. At higher levels, lead can cause permanent brain damage and even death[11]. Another study examined the leachability of heavy metals by traditional clay pots as cooking utensils in food stuffs in Rwanda and reported

2.692 µg/g (dry weight) of Pb in beans cooked in clay pot for 4 hours at 110 °C. Also, 0.192 µg/g of Pb were leached into tomato and carrot sauces that were cooked according to traditional recipes in Rwanda at the pH (4.4) of the food stuff[12].

It is against this background that this study assessed lead, arsenic, cadmium and mercury levels in the earthenware clay deposits at Mankessim in Mfantsiman District, of Ghana.

Experimental

Mankessim, the study area, is located within the Mfantsiman District with Saltpong as its district capital. The Mfantsiman District lies between latitudes 5° to 5°20' north and longitudes 0°44' to 1°11' west. The district is low lying with loose quaternary sands along the coast and is characterized by undulating coastal dense scrub and grassland with isolated marshy areas[13].

The Mfantsiman District is about 60 metres above sea level and drained by a number of rivers and streams including the Nkasaku, which empties into the Atufa lagoon in Saltpond and Aworaba which drains into Etsi lagoon in Kormantse[13].

The municipality is endowed with rich natural resources including talc, granite, silica and kaolin of commercial grade which are used in building construction and the ceramics industry. The vegetation consists of dense scrub tangle and grass, which grow to an average height of about 4.5 m. The Mfantsiman District has an average temperature of about 24 °C and relative humidity of about 70%, with double maximum rainfall, with peaks in May-June and October[13].

Sampling

Ten clay samples were taken from earthenware clay deposits at three sampling periods at Mankessim in the central region of Ghana in September, 2016. At each sampling site, composite samples made up of five sub-samples were taken from different locations, using the auger from a depth of 0.3 metres. A representative sample was taken from the composite samples for analysis. The samples were put into clean transparent polythene bags and labelled M_n where n=1-10. The samples were freed of pieces of roots, leaves, pebbles and other foreign objects by hand picking. The soil samples were dried in an oven at 60 °C to a constant weight. The dried samples and the control sample were ground and homogenized in a porcelain mortar, sieved to 0.5 mm mesh size and packed into the respective well labelled polythene bags for acid digestion.

About 2.0 g of each aggregate clay samples (five replicates) were transferred into 100 mL polytetrafluoroethylene (PTFE) Teflon bombs. Ten millilitres (10 mL) of concentrated nitric acid was added to the soil samples and allowed to stand for 10 minutes. About 30% H_2O_2 was also added to the mixture until the mixture no longer effervesced on addition of H_2O_2. To each mixture in the Teflon bombs, 2 mL of concentrated H_2SO_4 and then 5 mL of concentrated $HClO_4$ were added successively. The resulting mixtures were digested for 25 minutes in a Milestone microwave oven (Ethos 900) using the following operation parameters; 250 W for 2 min, 0 W for 2 min, 250 W for 6 min, 400 W for 5 min, 650 W for 5 min and 5 min for venting[14]. The rotor was put in a bowl of water to cool the content of the tube and also to reduce the associated pressure. The digested soil samples were filtered using Whatman No 1 filter paper into a 50 mL volumetric flask and made up to the mark using de-ionized distilled water. The chemicals used were analytical grade chemicals obtained from Sigma Aldrich.

The calibration standards for Cd, Pb and As, were prepared and together with the reagent blanks, subjected to the same digestion procedure as the samples. Subsequently, the digested standards, reagent blanks and samples were read at the wavelengths of 228.8 nm, 217 nm and 193.7 nm, using AAS, model AA240FS for the determination of Cd, Pb and As respectively in the digested clay samples. Acetylene gas was used as the carrier gas, for Cd, Pb and As while inert argon was pass through the system to remove interfering gases between each reaction time.

Samples for Hg were digested by adding 5.0 mL of H_2SO_4 followed by 2.5 mL of HNO_3 and 15.0 mL of freshly prepared 5 %(w/v) $KMnO_4$. The mixtures were made to stand for at least 15.0 minutes after which 8.0 mL of 5%(w/v) $K_2S_2O_8$ solution was added and digested for 25.0 minute using the operation parameters outlined earlier for Pb, As and Cd. The samples were decolourise by adding 10% hydroxylamine hydrochloride solution. A blank and calibration standards were prepared. Cold vapour was used for Hg determination using 3% HCl in 1.1% $SnCl_2$ and 3% HCl as the reductant at a wavelength of 253.7 nm[15].

Results and Discussion

The precision and accuracy of the AAS method was evaluated by analysis of standard reference material IAEA soil-7. Table 1 shows the recommended values for As, Cd, Pb, Hg, Cu, Al, Co and Ba in the standard as against the experimental values obtained using AAS. The values obtained compared favourably well with the recommended values as Spearman's correlation coefficient was +0.94. The experimental values were within ±6% of the recommended values. The measurement precision specified by the relative standard deviation was within ±5%. The error margins are standard deviations. The mean concentrations of As, Pb, Cd and Hg in earthenware clay samples are presented in Table 2 whilst Figure 1 is a graph showing the distribution of the various elements measured in the clay samples.

Table 1. Analytical results (µg/g dry weight) of standard reference materials, IAEA SOIL-7 showing observed values and recommended value, n=5 ('n' is no of readings from which the mean value was calculated)

Element	Recommended value[16]	Observed value
Hg	0.04±0.01	0.036±0.02
Cu	11.0±2.0	11.21±3.84
As	13.08±0.8	12.96±1.21
Pb	60.0±5.12	61.01±4.42
Co	8.90±1.2	8.60±2.1
Cd	1.3±0.2	1.28 ±0.01

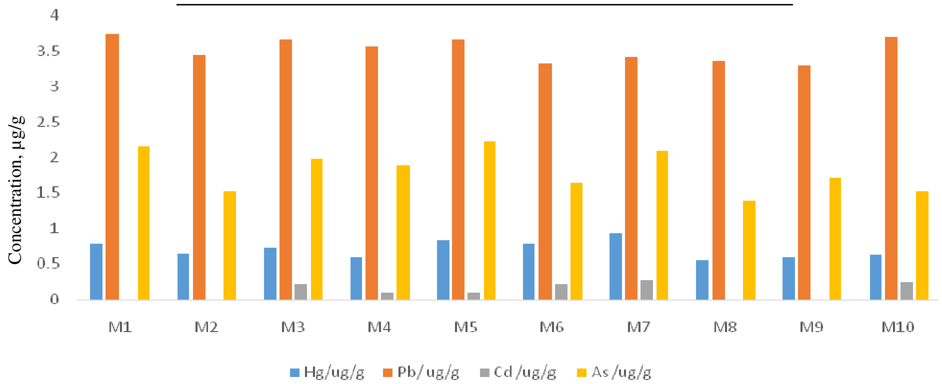

Figure 1. The distribution of Hg, Pb, Cd and As in clay samples at Mankessim

Lead concentration ranged from 3.30 µg/g to 3.75 µg/g with a mean of 3.52 µg/g and a standard deviation of 0.17 (Table 2). These levels were within the safe levels of 80.0 µg/g[17]. One study observed a mean of 6.5 µg/g of Pb in geophagy soil in Tanzania[6], while another study also reported 27.70±2.90 µg/g of Pb in geophagic white clay at Abuakwa in the Ashanti region of Ghana[18]. The lead levels in the samples from Mankessim were lower than the levels reported from other regions, where the clay is eaten directly. The Pb levels in Mankessim clay deposits were however, higher than the leachable levels of 2.692 µg/g reported in cooked bean[12].

Arsenic in the clay deposits ranged from 1.38 µg/g to 2.22 µg/g with a mean of 1.81 µg/g and a standard deviation of 0.30 (Table 2). The mean As level of 1.81 µg/g was over 25 times higher than the safe level of 0.07 µg/g of As in soil[17]. The higher level of As in the clay deposits in Mankessim are of much concern, as arsenic has a higher tendency to be leached into food stuff cooked in these traditional pots at high temperatures, low pH and long contact time of heat (cooking). Arsenic can pass through the food chain and impact negatively on human health. One study reported 5.8µg/g, 10.6 µg/g and 3.9 µg/g of As in geophagy clays in Accra, Abidjan and Nigeria respectively[7]. The reported levels in geophagy clays were even higher than the levels in clay deposits at Mankessim. Another study also reported 3.920±1.90 µg/g of As in edible clay obtained from Enyigba village, in Nigeria[2].

Cadmium concentrations in Mankessim clay deposits ranged from 0.09 µg/g to 0.27 µg/g with a mean of 0.11 µg/g and a standard deviation of 0.11 (Table 2). Cadmium was below the method's detection limit of 0.002 µg/g at sites M_1, M_2, M_8 and M_9 respectively. The levels of Cd observed in the study sites were below the safe level of 17.0 µg/g of Cd[17]. However, these levels were lower than 3.654 µg/g and 1.731 µg/g of Cd leachates from traditional clay pots in which beans and tomato sauces were cooked for 4 hours at 110 °C and pH (4.4) of food stuff[12].

Table 2. Mean concentrations (µg/g dry weight) of As, Pb, Cd and Hg in clay soil, n=5

Sample code	Hg/µg/g	Pb/µg/g	Cd /µg/g	As /µg/g
M_1	0.78	3.75	<0.002	2.16
M_2	0.65	3.44	<0.002	1.52
M_3	0.72	3.66	0.21	1.98
M_4	0.60	3.57	0.09	1.89
M_5	0.84	3.66	0.09	2.22
M_6	0.78	3.33	0.21	1.65
M_7	0.93	3.42	0.27	2.10
M_8	0.54	3.36	<0.002	1.38
M_9	0.60	3.30	<0.002	1.71
M_{10}	0.63	3.69	0.24	1.53
Statistics				
Min	**0.54**	**3.30**	**0.09**	**1.38**
Max	**0.93**	**3.75**	**0.27**	**2.22**
Mean	**0.71**	**3.52**	**0.11**	**1.81**
Median	**0.69**	**3.51**	**0.09**	**1.80**
SD	**0.12**	**0.17**	**0.11**	**0.30**
US EPA(1990) safe levels	**18.0**	**80.0**	**17.0**	**0.07**

NB: < 0.002 means below the detection limit of 0.002 µg/g, 'n' is no. of readings

The concentration of Hg ranged from 0.54 µg/g to 0.93 µg/g with a mean of 0.71 µg/g and a standard deviation of 0.12 (Table 2). These levels were within the safe levels of 18 µg/g[17].

Mercury was observed in all the samples analysed. These levels of Hg might be lower in the end product as the metal has the tendency to evaporate during the firing process because of high volatility of Hg at higher temperatures. However, other studies reported as high as 2.4 µg/g, 1.4 µg/g and 1.5 µg/g of Hg in Accra, Abidjan and Nigeria, geophagy clays, which are eaten directly[7], as well as a mean of 0.53 µg/g in clay deposits in Vume in the Volta region of Ghana[5] and a mean concentration of 0.046 µg/g of Hg in geophagy soil in Tanzania[6].

Conclusion

Although, arsenic levels in the Mankessim clay deposits were higher considering the safe level of 0.07 µg/g of As[16], the concentrations of As can be said to be reasonably good,as these levels were even lower than the reported levels in geophagy clay in other part of Ghana and elsewhere. However, cooking, grinding and storage of food stuff in end products of Mankessim clay at low pH, higher temperatures and long cooking period (contact time) could lead to leachable arsenic into prepared food which can have health implications as arsenic is very toxic. In general, Hg, Pb and Cd were all below the acceptable limit[17]. Hence, some remediation interventions should be put in place by potters in order to reduce As levels before it is used to produce food wares.

Acknowledgement

The author expressed his appreciation to Mr Bobobee, a colleague at the Chemistry Education department, University of Education, Winneba for reading the manuscript and making important suggestions.

References

1. **A**mponsah-Dacosta F, Muzerengi C, Mhlongo S E and Mukwevho, *ARNP J Engg Appl Sci.,* 2013, **8(11),** 927-932.
2. Ogah S P I and Ikelle I I, *Der Pharma Chemical,* 2015, **7(11),** 264-267.
3. USGS, Environmental Characteristics of Clay and Clay Mineral Deposits, USGS Information Handout, 1999; https://pubs.usgs.gov/info/clays/
4. Manukaji J U, *Am J Engg Res.,* 2013, **2(4),** 33-38.
5. Samlafo B V, Bobobee L H, Quarshie E and Sarsah L A, *Int J Current Res.,* 2016, **8(11),** 42230-42233.
6. Nyanza E C, Joseph M, Premji S S, Thomas S K D and Mannion C, *BMC Pregnancy Child Birth,* 2014, **14**, 144-154; DOI:10.1186/1471-2393-14-144
7. Woode A and Hackman-Duncan S F, *Canadian J Pure Appl Sci.,* 2014, **8(1),** 2789-2794.
8. WHO, Arsenic and Arsenic Compounds Environmental Health Critaria 224, Geneva, 2001, 12-45.
9. WHO, Concise International Chemical Assessment Document 50. IPCS: Human Health Aspects, Geneva, 2003, 24-56.
10. Yu N, *Annals of Agrarian Sci.*, 2016, **14**, 257-263
11. Gagan F, Deepesh G and Archana T, *Interdiscip Toxicol.,* 2012, **5**(**2**), 47-58; DOI:10.2478/v10102-012-0009-2
12. Nsengimana H, Munyentwali A, Muhayimana P and Muhizi T, *Rwanda J.,* 2012, **25**, 52-65; DOI:10.4314/rj.v25i1.4
13. Ghana Statistical Service, Population and Housing Census, District Analytical Report, Mfantsiman District, Accra, 2014, 1-10, http://www.statsghana.gov.gh/

14. Milestone S L, Milestone Technical Paper: Microwave Acid Digestion Cookbook. Milestone Lab Systems, 2001, 20-56.
15. APHA, Standard Methods for the Examination of Water and Wastewater, 18^{th} Edn., American Public Health Association, 1992.
16. Trace Elements in Soil, Reference Material, IAEA-SOIL-7, International Atomic Energy Agency, Analytical Quality Control Service, Austria, January 2000.
17. US, EPA 1990, Safe levels-Heavy metals and gardens, Retrieved from: https://sites.google.com/site/healthygardeners/safe-levels
18. Nkansah M A, Korankye M, Darko G and Dodd Matt, *Toxicology Reports,* 2016, **3,** 644-651; DOI:10.1016/j.toxrep.2016.08.005