

Arsenic and Mercury Levels in Earthenware Clays in Otsew in Gomoa West District of Central Region of Ghana using Instrumental Neutron Activation Analysis

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Abstract: This study was conducted to investigate the occurrence and extent of potentially toxic heavy metals, As and Hg in earthenware clay deposits at Otsew in the Gomoa West District of the Central Region of Ghana using the Instrumental Neutron Activation Analysis (INAA) technique. Arsenic concentrations in the clay ranged from 1.55 ± 0.23 to 18.47 ± 2.60 $\mu\text{g/g}$ at S_6 and S_{10} respectively with a mean of 9.48 $\mu\text{g/g}$. Arsenic was not detected in sample S_3 . Mercury concentration in the clay ranged from 0.030 ± 0.005 to 0.31 ± 0.01 $\mu\text{g/g}$ in S_2 and S_3 respectively, with a mean of 0.14 $\mu\text{g/g}$. Mercury was however, not detected in S_{10} . The precision and accuracy of the analytical technique (INAA) were assessed by simultaneous activation of reference material IAEA soil-7. The values obtained compared favourably well with the recommended values as Spearman's correlation coefficient was $+0.99$. The experimental samples were within $\pm 5\%$ of the recommended values. The measurement precision specified by the relative standard deviation was within $\pm 4\%$.

Key words: Clay, element, food, level, recommended, toxic

INTRODUCTION

Pottery is known to be one of the most ancient craft and first synthetic material to be discovered by man (Anquanda, 2008). The pepper-grinding bowls popularly called *ayiwa* by the Akans and *wegba* by the Ewes is made by traditional potters. These bowls and pots are functional products in most Ghanaian homes for grinding of pepper, cooking and water storage (Anquanda, 2008). Even Ghanaian kings and queens eat from these bowls. Pots and pepper grinding bowls are low fired, therefore fragile, but inexpensive and environmentally friendly compared to its modern plastic types which are not biodegradable, and therefore environmentally unfriendly (Anquanda, 2008). These pots and bowls are on sale in every market and often on the roadsides where clay deposits are located. Pots are still used to prepare, cook, and store food.

Traditional potters in Ghana do not perform any chemical analysis on earthenware clays from clay deposits

before using the clay for commercial production of pots and pepper-grinding bowls. All they look out for in terms of the suitability of the clay for making pots and pepper-grinding bowls is its plasticity. Consequently, if the geochemistry of the clay has high levels of heavy metals above the recommended levels, then the quality of these products becomes questionable as these elements have a higher tendency to enter the human body through food. Moreover, these bowls serve as utensils for cooking, drinking and storing food and water. With continuous grinding, the ridges in a typical *ayiwa* or *wegba* that facilitate the grinding process wears out and as a result, there is a high tendency that any harmful element present in the clay will leach into the food and eventually enter the human body. The pots are still used in Ghanaian homes for cooking and storage of water (Anquanda, 2008).

Arsenic is found in the earth's crust at an average level of 2 mg/kg . Most natural soils contain low levels of arsenic, but industrial wastes and pesticide applications

may increase concentrations. Background concentrations in soil range from 1 to 40 mg/kg, with a mean value of 5 mg/kg (Chatterjee, 1999). Chatterjee and Mukherjee (1999) reported arsenic levels of 20100-35500 mg/kg in soil around the effluent dumping point of an arsenical pesticide manufacturing plant

The amount of arsenic sorbed from solution increases as the free iron oxide, magnesium oxide, aluminium oxide or clay content of the soil increases. Removal of amorphous iron or aluminium components by treatment with oxalate eliminates or appreciably reduces the arsenic sorption capacity of the soil. Under reducing conditions, arsenite dominates in soil (Haswell *et al.*, 1985). The surfaces of aluminium oxides/hydroxides and clay may play a role in arsenic adsorption, but only in acidic soils.

Elfving *et al.* (1994) monitored the movement of arsenic following the application of lead arsenate to fruit orchards for insect control. The rate of decrease in concentration of arsenic with depth was significantly greater in a sandy soil than in clay, suggesting that downward movement occurred less readily in the former. The use of phosphate fertilizers significantly increases the amount of arsenic leached from soil contaminated with lead arsenate pesticide residues (Davenport and Peryea, 1991).

Trivalent inorganic arsenicals, such as arsenite, readily react with sulfhydryl groups such as cysteine (Delnomdedieu *et al.*, 1994). The complex between arsenic and vicinal sulfhydryl reagent is particularly strong. The activity of enzymes or receptors is due in part to the functional groups on amino acids such as the sulfhydryl group on cysteine or coenzymes such as lipoic acid, which has vicinal thiol groups. Thus, if arsenite binds to a critical thiol or dithiol, the enzyme may be inhibited (Aposhian, 1989). Arsenite inhibits pyruvate dehydrogenase, a lipoic-acid-dependent enzyme involved in gluconeogenesis. The acute toxicity of inorganic arsenic may result in part from inhibition of gluconeogenesis and ultimately depletion of carbohydrates from the organism. However, binding of arsenite to protein at non-essential sites may be a detoxification mechanism (Aposhian, 1989).

A mechanism of toxicity of pentavalent inorganic arsenic, such as arsenate, is its reduction to a trivalent form, such as arsenite. The reduction of arsenate to arsenite occurs *in vivo*. Arsenite is more toxic than arsenate, as evidenced by the lower amount of it needed to elicit a toxic response.

Another potential mechanism is the replacement of phosphate with arsenate. IPCS (2001) reported that in the human erythrocyte, arsenate can replace phosphate in the sodium pump and the anion exchange transport system.

Arsenate can form esters with glucose and gluconate (Gresser, 1981), forming glucose-6-arsenate and 6-arsenogluconate, respectively. These compounds resemble glucose-6-phosphate and 6-phosphogluconate. Glucose-6-phosphate and glucose-6-arsenate have similar V_{max} values as substrates for glucose-6-phosphate dehydrogenase and each can inhibit hexokinase.

The average mercury concentration in surface soil is reported to be from 20 to 625 $\mu\text{g}/\text{kg}$ (Reimann and de Caritat, 1998). Higher concentrations are reported in soils from urban locations and close to sources of Hg pollution.

The transformation processes for the various forms of mercury that apply in water also occur in soil and sediment. Formation and breakdown of organic mercury compounds appear to be dependent upon the same microbial and abiotic processes as in water (Andersson, 1979), and the methylation of mercury is decreased by increasing chloride ion concentration (Olson *et al.*, 1991), although the presence of chloride ions has been suggested to increase the rate of mercury release from sediments (Wang *et al.*, 1991). In soil, the complexing of elemental mercury with chloride ion and hydroxide ion to form various mercury compounds is dependent upon pH, salt content, and soil composition.

The central nervous system is probably the most sensitive target for elemental mercury vapour exposure. Similar effects are seen after all durations of exposure; however, the symptoms may intensify and/or become irreversible as exposure duration and/or concentration increase (IPCS, 2003). A wide variety of cognitive, personality, sensory, and motor disturbances have been reported. Prominent symptoms include tremors (initially affecting the hands and sometimes spreading to other parts of the body), emotional disturbances (characterized by irritability, excessive shyness, confidence loss, and nervousness), insomnia, memory loss, neuromuscular changes and performance deficits in tests of cognitive function. Some long-term exposures to elemental mercury vapour have resulted in unsteady walking, poor concentration, tremulous speech, blurred vision, performance decrements in psychomotor skills (IPCS, 2003).

This study, examines the levels of some harmful elements such as arsenic and mercury in the earthenware clay deposits at Otsew in the Gomoa West District of the Central region of Ghana.

MATERIALS AND METHODS

A total of ten (10) soil samples were taken from earthenware clay deposits at Otsew in the Gomoa West District in the Central Region of Ghana, in November,

2010. At each sampling site, a composite sample made up of five (5) sub-samples, taken from different locations, was taken using the Auger from a depth of 30 cm. A representative sample was taken from the composite sample to the laboratory for analysis. The samples were put into a clean transparent polythene bags and labelled S_n , where $n = 1-10$. A pepper-grinding bowl (ayiwa) bought from the Winneba market was used as the control sample.

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 irradiation.

Five sub-samples of 100 mg of each sample were weighed and wrapped into transparent polyethylene films together with an identification codes and heat sealed. The same mass of single Hg and As comparator standards were also weighed and heat sealed. A standard reference material IAEA soil-7 was similarly treated as the samples and heat sealed. The heat sealed samples were packed into a medium size vials for irradiation. The standard reference material IAEA soil-7 was used as quality control to validate the analytical technique.

Irradiation and counting of samples using the Ghana Research Reactor-1 facility has been described earlier (Nyarko, 2003). The packed soil, standard reference material and the comparator standards were irradiated at the inner irradiation sites of the Reactor-1 facility, using a pneumatic transfer system for 1 h at a thermal neutron flux 5×10^{11} n.cm²/s and a pressure of 1.723 bars, allowed to decay for 24 h and counted for 600 sec. The irradiation time (t_i), decay time (t_d) and counting time (t_c) were chosen according to half-life of the radionuclides of interest, and the sample matrix as well as the safe handling of radioactive samples.

The counting of samples was done using a gamma-ray spectroscopy system. The system was made up of N-type HPGe detector model GR2518, and HV Power Supply Model 3103, a spectroscopy Amplifier Model 2020, an ACCUSPEC Multi-channel Analyzer (MCA) emulation software card, all manufactured by Canberra Industries, Inc, and 486 micro-computer. The efficiency of the detector was 25%. Each sample was placed at a distance of 2.6 cm from the detector surface and counted. The accumulated spectra intensities were analyzed qualitatively and quantitatively. The qualitative analysis involved the identification of As using the 559.1 keV of ⁷⁶As and Hg using 77.4 keV of ¹⁹⁷Hg. The quantitative

analysis was done by converting the counts (area) under the photopeak of the radionuclides by comparator INAA (Nyarko, 2003) method using pure As and Hg single standards. Cobalt-60, Caesium-137 and Barium-133 sources were used to calibrate the detector periodically whenever counting was going to be done and between counting of the samples.

RESULTS AND DISCUSSION

The precision and accuracy of the analytical technique (INAA) were assessed by simultaneous activation of reference material IAEA soil-7. Table 1 shows the analytical results obtained for As, Ba, Br, Al, K, Cu, La, Mn Na, and Sc at GHARR-1 laboratory for the reference material compared with the experimental samples. The values obtained compared favourably well with the recommended values as Spearman's correlation coefficient was +0.99. The experimental samples were within $\pm 5\%$ of the recommended values. The measurement precision specified by the relative standard deviation was within $\pm 4\%$. The error margins are standard deviations.

The mean concentrations of As and Hg in earthenware clays are presented in Table 2. Arsenic concentrations in the clay ranged from 1.55 ± 0.23 to 18.47 ± 2.60 $\mu\text{g/g}$ at S_6 and S_{10} , respectively with a mean of 9.48 $\mu\text{g/g}$. Arsenic was not detected in sample S_3 . The control sample bought from the market, C_1 , recorded a value of 6.73 ± 1.0 $\mu\text{g/g}$ of As. These levels of As observed in the clay are much higher than the acceptable level of 5.0 $\mu\text{g/g}$ in both the experimental and the control samples (Fig. 1). The levels of As in this clay deposit might be due to the periodic flooding and run-off from agricultural farmlands as these flood waters and run-off might contain As residue from application of pesticides and fertilizers to food crops, since the deposit is a marshy area.

Table 1: Analytical results ($\mu\text{g/g}$) of standard reference material, IAEA soil-7 showing local laboratory values and the recommended values

Elements	Concentration levels	
	IAEA standard values/ $\mu\text{g/g}$	Experimental values/ $\mu\text{g/g}$
As	13.4 \pm 0.8	12.86 \pm 1.21
Ba	159 \pm 32.0	176 \pm 25.2
Br	7.0 \pm 3.0	6.8 \pm 3.2
Ca (%)	16.0 \pm 1.0	19.1 \pm 2.5
Al	4.7 \pm 0.3	4.2 \pm 0.05
K	1.2 \pm 0.1	1.4 \pm 0.02
Cu	11.0 \pm 2.0	12.8 \pm 3.21
La	28.0 \pm 1.0	26.89 \pm 2.54
Mn	631.0 \pm 22	625.4 \pm 6.0
Na	0.24 \pm 0.02	0.21 \pm 0.01
Sc	8.3 \pm 0.1	8.8 \pm 0.5

Table 2: Mean concentrations ($\mu\text{g/g}$) of As and Hg in clay soil

Sample code	As/ $\mu\text{g/g}$	Hg/ $\mu\text{g/g}$
S ₁	9.08±1.36	0.11±0.02
S ₂	10.40±1.53	0.03±0.01
S ₃	ND	0.31±0.01
S ₄	15.76±2.36	0.19±0.03
S ₅	9.72±1.45	0.21±0.03
S ₆	1.55±0.23	0.06±0.01
S ₇	12.23±2.02	0.21±0.03
S ₈	4.49±0.67	0.17±0.02
S ₉	13.09±2.19	0.06±0.01
S ₁₀	18.47±2.60	ND
C ₁	6.73±1.0	0.19±0.02

ND: not deducted

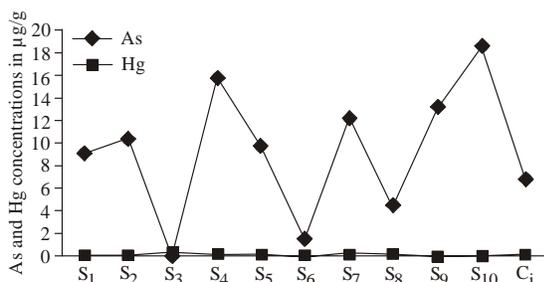


Fig. 1: Variations of As and Hg concentrations in clay

Amonoo-Neizer and Amekor (1993) reported that uncontaminated soils were found to contain arsenic levels between 0.2 and 40 mg/kg, whereas arsenic-exposed soils contained up to 550 mg/kg. Soil levels in excess of 200-300 mg/kg are necessary for plants to absorb sufficient arsenic to reach edible plant levels of 1 mg arsenic/kg fresh mass. Although, the levels observed in the study area might be good for agricultural activities, it may be dangerous for products such as the grinding bowls. This is because food is prepared directly from these bowls and there is a high tendency that As in these bowls will enter the human body along with food.

Hayford *et al.* (2008) reported a range of 0.62-14.35 $\mu\text{g/g}$ of As in mining impacted areas of Tarkwa-Prestea Soil. In other countries (Canada, UK, Netherlands and Australia), the standard for As in Agricultural soils is generally in the range 10-20 ppm.

Mercury concentrations in the clay ranged from $(3.0 \pm 0.5) \times 10^{-2}$ to $0.31 \pm 0.01 \mu\text{g/g}$ in S₂ and S₃ respectively, with a mean of $0.14 \mu\text{g/g}$. Mercury was however, not detected in S₁₀. The control sample C₁ recorded $0.19 \pm 0.02 \mu\text{g/g}$ of Hg. The Hg levels were generally low and could escape during the firing process since Hg is very volatile.

Hayford *et al.* (2008) reported a range of 0.22-0.59 $\mu\text{g/g}$ of Hg in the Tarkwa-Prestea area while the permitted level was set at $5.0 \mu\text{g/g}$ of Hg. Sullivan *et al.* (2006) reported an average of $0.032 \mu\text{g/g}$ at coal fired power

plants at Springfield. The standard for the world background level was set at 0.02-0.41 $\mu\text{g/g}$ while the US set 0.04-0.28 $\mu\text{g/g}$ of Hg as its background standard. Comparing the standard set for the world background to the observed values, it can be concluded that the Clay deposit at the study site is within the level of world standard of mercury concentration in soil, hence a good clay deposit for earthenware clays.

CONCLUSION

Arsenic levels in earthenware clays in the study area were a little higher considering the fact that food is either prepared or cooked directly in them. Hence some remediation interventions should be put in place in order to reduce As levels in the clay before it is used to produce earthenware products. Mercury levels in the Clay were within acceptable limit. However, the earthenware products should be well fired in order to reduce Hg levels to the lowest minimum, since Hg has the tendency to evaporate at high temperatures.

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REFERENCES

- Amonoo-Neizer, E.H. and E.M.K. Amekor, 1993. Determination of Total Arsenic in Environmental Samples from Kumasi and Obuasi. Ghana Environ. Health Persp., 101(1): 46-49.
- Andersson, A., 1979. Mercury in Soils. In: Nriagu, J.O. (Ed.), The Biogeochemistry of Mercury in the Environment. Elsevier/North Holland Biomedical Press, New York, pp: 79-112.
- Anquanda, J.A., 2008. The Traditional Potter's Craft. National Commission on Culture. pp: 1-5. Retrieved from: www.ghanaculture.gov.gh, (Accessed on: January 18, 2000).
- Aposhian, H.V., 1989. Biochemical Toxicology of Arsenic. In: Hodgson, E., J.R. Bend and R.M. Philpot, (Eds.), Reviews in Biochemical Toxicology. Vol. 10, Elsevier Science, New York.
- Chatterjee, A. and A. Mukherjee, 1999. Hydrogeological investigation of ground water arsenic contamination in South Calcutta. Sci. Total Environ., 225(3): 249-262.
- Davenport, J.R. and F.J. Peryea, 1991. Phosphate fertilizers influence leaching of lead and arsenic in a soil contaminated with lead arsenate. Water Air Soil Pollut., 58: 101-110.

- Delnomdedieu, M., M.M. Basti, J.D. Otvos and D.J. Thomas, 1994. Reduction of binding of arsenate and dimethylarsinate by glutathione: a magnetic resonance study. *Chem. Biol. Interact.*, 90: 139-155.
- Elfving, D.C., K.R. Wilson, J.G. Ebel, K.L. Manzell, W.H. Gutenmann and D.J. Lisk, 1994. Migration of lead and arsenic in old orchard soils in the Georgian Bay region of Ontario. *Chemosphere*, 29(2): 407-413.
- Gresser, M.J., 1981. ADP-arsenate, formation by submitochondrial particles under phosphorylation conditions. *J. Biol. Chem.*, 256: 5981-5983.
- Haswell, S.J., P. O'Neill and K.C. Bancroft, 1985. Arsenic speciation in soil-pore waters from mineralized and unmineralized areas of South-West England. *Talanta*, 32: 69-72.
- Hayford, E.K., A. Amin, E.K. Osae and J. Kutu, 2008. Impact of gold mining on soil and some staple foods collected from selected mining communities in and around Tarkwa-Prestea area. *W. Afr. J. Appl. Ecol.*, 14(1).
- IPCS, 2001. Arsenic and Arsenic Compounds, Environmental Health Criteria 224. WHO, Geneva, pp: 12-24.
- IPCS, 2003. Elemental Mercury and Inorganic Mercury Compounds: Human Health Aspects, WHO, Geneva.
- Nyarko, B.J.B., E.H.K. Akaho and Y. Serfor-Armah, 2003. Application of NAA standardization methods using a low power research reactor. *J. Radioanal. Chem.*, 275: 361-366.
- Olson, B.H., S.M. Cayless, S. Ford and J.M. Lester, 1991. Toxic element contamination and the occurrence of mercury-resistant bacteria in mercury contaminated soil, sediments, and sludges. *Arch. Environ. Con. Tox.*, 20(2): 226-233.
- Reimann, C. and P. de Caritat, 1998. Chemical Elements in the Environment. Facts Sheets for the Geochemist and Environmental Scientist. Springer.
- Sullivan, T., B. Bowerman and J. Adams, 2006. Mercury Emissions from Coal Fired Power Plants: Local Impacts on Human Health Risk, Brookhaven National Laboratory, December, 2005, BNL-75594-2006.
- Wang, J.S., P.M. Huang, W.K. Liaw and U.T. Hammer, 1991. Kinetics of the desorption of mercury from selected fresh water sediments as influenced by chloride. *Water Air Soil Pollut.*, 56: 533-542.