

## Investigation into Trace and Major Elements of “Hyire” (Kaolin) Widely used in Ghana Using Neutron Activation Analysis

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**Abstract:** This study was conducted to investigate the occurrence and extent of potentially trace and major elements in kaolin, widely used in Ghana, using the Instrumental Neutron Activation Analysis (INAA) technique. Soil plays a vital role in human sustenance on earth. Different forms of soil have been used over the years to solve pertinent requirements of man. Kaolin, commonly referred to as “hyire” in Ghana, has been used by women during the delicate periods of their pregnancy and also by lactating mothers. This study has sought to conduct an analysis of the toxic elements that may be ingested by these pregnant women when they eat “hyire” using Instrumental Neutron Activation Analysis (INAA) at the Ghana Research Reactor-1 facility. The study has shown that even though there are useful (major) elements present in the samples used, some toxic elements were also found to be beyond the Recommended Dietary Allowance for those elements. Recommendation has been made to request policy makers to regulate the production and use of “hyire” in order that pregnant women and their foetus are not exposed to effects of the toxic components detected. Industries have been encouraged to invest in this viable sector and to use modern technology to make the manufacturing of “hyire” more refined.

**Key words:** Heavy metals, instrumental neutron activation analyses, trace elements

### INTRODUCTION

Kaolin which is also known as “China clay”, is a natural claylike mineral (silicate of aluminum) and is composed of silica, iron, magnesium, calcium, sodium and other minerals.

Kaolin has also been used topically as an emollient and drying agent. Specifically, it has been used to dry oozing and weeping poison ivy, poison oak, and poison sumac lesions. It has also been used as a protectant for the temporary relief of anorectal itching and diaper rash.

Demand is most in the manufacture of paper where it performs two separate functions- as a filler to improve printing characteristics and as a coating pigment to enhance the surface properties of the paper such as the brightness, smoothness, gloss and ink receptivity etc. (Taylor, 1998)

In the ceramics industry the main function of kaolin is to impart whiteness. Its major uses are in vitreous china sanitary ware, table ware, wall tiles and electrical porcelain (Adamis and Williams, 2005).

Kaolin is used in refractories where it is valued for its alumina content. Performance mineral applications use

kaolin as fillers in paint, rubber, plastics and adhesives and sealants and pharmaceuticals. Other important uses include the manufacture of white cement and glass fibre (Adamis and Williams, 2005).

People around the world eat clay, dirt or other pieces of the lithosphere for a variety of reasons. Commonly, it is a traditional cultural activity which takes place during pregnancy, religious ceremonies, or as a remedy for disease. Most people who eat dirt live in Central Africa and the Southern United States. While it is a cultural practice, it also fills a physiological need for nutrients.

In Ghana, kaolin which is locally known as “hyire”, is chalk-like in nature and it is very popular with pregnant and lactating mothers as well as herbalists. The chalk can be bought in ethnic shops and markets in the form of blocks, pellets and powders (i.e., a variety of sizes and with differing content of minerals). There are no particular brands, batches or expiry dates. These “hyire” samples are prepared by the native people depending on what the sample will be used for. Some of them are burnt in an oven whilst others are dried in the sun to have a desired effect. It is traditionally consumed by the pregnant women as remedy of morning sickness. Certain

additives are added to the base material to enhance their potency. Pregnant and lactating women are able to satisfy the very different nutritional needs of their bodies by eating “hyire”. Traditionally, herbalists or native doctors use “hyire” for the cure of diarrhea and other ailments. It is necessary to investigate the composition of “hyire” because it is ingested for both nutritional and medical reason as any contamination might cause havoc.

The level of most of the constituents in various “hyire” samples used by many Ghanaians is unknown. Instrumental Neutron Activation Analysis (INAA) has been used to analyze the elemental composition of six different types of kaolin and their effects on the individuals who ingest them.

## MATERIALS AND METHODS

**Instrumentation:** Sample irradiations for neutron activation analysis were carried out in the 30 kW Miniature Neutron Source Reactor (MNSR) at a neutron flux of  $5 \times 10^{11}$  neutrons/cm<sup>2</sup>s. The reactor is situated at the Ghana Atomic Energy Commission, Kwabenyaa, Accra, Ghana.

**Study design:** “Hyire” samples were bought from the local market place as well as ethnic shops in Accra and Cape-coast for the study from June, 2010 to August, 2010. The samples were collected and placed in plastic container which had previously been treated with 10% nitric acid for 24 h and rinsed with de-ionised water. The samples were kept over ice in an ice chest transported to the laboratory and stored frozen at 4 degrees before use.

**Sample preparation:** The samples were ground to powder and homogenized. It was stored frozen and later freeze-dried to constant weight. 100 mg of each sample was weighed and packaged. Similarly, 100 mg of standard reference materials were weighed and packaged for irradiation. The samples were placed in small irradiation vials (diameter 1.6 cm and height 5.5 cm). The small irradiation vials containing the samples and standards were heat-sealed. Two standard reference materials with certified values were used to validate the INAA method. The reference materials were: IAEA-Soil-7 and NIST-SRM 1646a Estuarine Sediment. The samples were then sent for short, medium and long irradiations.

**Sample irradiation and counting:** Samples and standards were transferred into the reactor via the pneumatic transfer system at a pressure of 0.6 MPa. The “hyire” samples were irradiated for 10s (for the short lived radionuclides), 30 min (for the medium lived radionuclides) and 1h (for the long lived radionuclides) (IAEA-TECDOC-564, 1990). At the end of the irradiation, the samples and standards were removed from

the reactor and allowed to decay for 1min (for short), 24 h (for medium) and 2 wks (for long) respectively. The small irradiation vial containing the radioactive kaolin sample was placed on the coaxial High Purity Germanium (HPGe) semi-conductor  $\gamma$ -ray detector (Canberra) and the  $\gamma$ -activity of the induced radioisotopes were measured. Measurement time depended on the activities of the induced radioisotopes. Similarly, measurement of the  $\gamma$ -activity of the induced radioisotopes produced in the standard reference material was obtained on the same coaxial HPGe  $\gamma$ -ray detector (and at the same source-detector distance). A plexiglass source support was mounted on the detector during the measurement in order to ensure easy and reproducible source positioning (De-Corte *et al.*, 1987). The ORTEC MAESTRO-32  $\gamma$ -spectroscopy software was used for  $\gamma$ -spectrum acquisition.

## RESULTS AND DISCUSSION

The precision and accuracy of the analytical technique (INAA) were assessed by simultaneous activation of reference material IAEA soil-7 and NIST-SRM 1646a Estuarine Sediment. Table 1 shows the analytical results obtained for Al, As, Ca, Co, Fe, K, Mg, Mn, Na, Sc, Ti and V at GHARR-1 laboratory for the reference materials compared with the experimental samples. The values obtained compared favourably well with the recommended values. 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 sample identifications were chosen based on the specific use of the kaolin; the samples were labeled RT, PB, PE, FT, EP and RG respectively. The samples RT, PB and PE are all various varieties of kaolin that are eaten. The samples FT and RT are basically used for medication by native doctors and herbalists. However, the sample label EP is eaten and used for medication as well. The results obtained recorded essential elements (Na, Mg, V, Al, Ca, K, Fe and Mn) and other toxic elements like As, Ti, Co and Sc. Twenty-one inorganic elements made up of 6 major minerals (Ca, Na, K, Mg, P and Cl) and 15 trace elements (As, Co, Cr, Cu, F, Fe, I, Mn, Mo, Ni, Se, Si, Sn, V and Zn) are now considered as being essential to human life. Each major mineral is required in several hundred milligrams/day while the traces are required in few milligrams daily (Linder, 1991). Table 2 describes the mean values of elemental concentrations of the kaolin samples with standard deviations

The levels of Mg in the kaolin sample were highest for the samples that are used singularly for medication and were lowest for the sample PB which is eaten.

Table 1: Analytical results and recommended values of IAEA-SOIL 7, and NIST-SRM 1646a Estuarine Sediment certified reference materials (mg/kg)

Element	IAEA-SOIL 7		NIST-SRM 1646a Estuarine Sediment	
	reported	This study	reported	This study
Al	47000 <sup>#</sup>	46582	22970±180	22950±160
As	13.4*	12.9	6.23±0.21	6.18±0.19
Ca	163000 <sup>#</sup>	164020	5190±200	5168±195
Co	8.9*	8.6	5*	6
Fe	25700 <sup>#</sup>	24991	20080±390	20078±395
K	12100 <sup>#</sup>	11800	8640±160	8710±140
Mg	11300 <sup>#</sup>	11600	3880±90	3900±98
Mn	631*	646	234.5±2.8	242±3.2
Naz	2400 <sup>#</sup>	2375	7410±170	7500±200
Sc	8.3*	7.9	5*	4
Ti	3000 <sup>#</sup>	2980	4560±210	4615±197
V	66*	68	44.84±0.76	44.64±0.63

\*: Non certified/recommended value, #: Information value

Table 2: Mean values of elemental concentrations of the Kaolin samples with standard deviations (mg/kg, unless indicated otherwise)

Elements	SampleID					
	RG	FT	RT	PB	EP	PE
Mg	13448±4825	7379±4646	2967±1348	955.80±143.37	1437±215.55	9430±364.8
V	60.16±9.57	0.89±0.1335	13.93±2.0895	127.71±10.41	52.23±9.86	141.55±11.45
Al	95547±508	82.75±36.13	2815±60.83	73879±429.42	48462±224.09	82268±354.63
Mn	ND	14.96±2.244	ND	ND	399.72±58.57	821±123.15
Ca	2958±443.7	1450±217.5	287.09±43.058	308±46.2	956.97±143.546	669.88±100.48
Na	11421±28.89	2169±12.36	376.1±7.11	600.88±8.21	3675±18.5	562.83±7.82
K	20401±530.14	21116±400.52	34328±488.78	35123±502.83	35575±642.52	31425±47.13
As	ND	7.48±2.6	617.44±2.53	18.53±2.71	1.78±0.267	ND
Ti	2088±704	ND	1826±414	3336±796	2178±844	6624±993.6
Sc	4.16±0.22	5.48±0.24	9.47±0.29	ND	8.30±0.29	9.38±0.32
Co	2.95±0.12	0.86±0.129	0.27±0.041	ND	28.67±2.83	0.71±0.107
Fe	0.87±0.19	1.88±0.28	0.97±0.20	ND	276575±3157	2.46±0.45

ND: Not-detected

However, the values obtained for all the samples were higher than the Recommended Dietary Allowance (RDA) of 420 mg (RDA, 1989). The high levels of Mg are desirable as it is needed in the body for the secretion of several enzymes.

Generally, the levels of V in the kaolin samples were relatively low as compared to the other elements. The level of V was highest in sample PE (which is eaten by pregnant women) and lowest in sample FT (which is also a variety that is used for medication). Vanadium has established, albeit specialized, biochemical roles as structural or functional cofactors in other organisms. This element appears not to be utilized by humans (Lippard and Berg, 1994)

Aluminium levels range from 95547±508 mg/kg in RG to 82.75±36.13 mg/kg in FT. The levels are fairly high in the samples

Manganese levels were not detected in some of the samples. However, other samples recorded values of 14.96±2.244 mg/kg (being the least), 399.72±58.57 and 821±123.15 mg/kg. These values represent a variety of sample that are eaten and also used for medication. The RDA for Mn is 2.3 mg indicating that the Mn concentrations obtained in these samples are way above this value. Even though, Mn is a cofactor in enzyme functions, an excess of it could cause manganism.

The sample labeled RG has the highest level of Ca (2958±443.7 mg/kg) and RT has the lowest level of Ca (287.09±43.058 mg/kg). All the other samples had some concentration of Ca which is essential for strong bones and teeth. Some of the concentrations obtained are less than the RDA of 1000 mg, however, continual intake of these samples could increase the concentration of calcium in the body.

Sodium levels also ranged from 376.1±7.11 to 11421±28.89 mg/kg. The Na levels in some of the samples were below the RDA which is 1500 mg, but higher in RG, FT and EP. Sodium is a systemic electrolyte and is essential in co regulating ATP with potassium (Nelson and Michael, 2000). Continual use will lead to bioaccumulation thereby providing the RDA.

The kaolin samples have the very high levels of potassium (20401±530.14 - 35575±642.52 mg/kg). The RDA for potassium is 4700 mg which is way below the values recorded in the sample. This is an indication that the intake of any of the kaolin samples can assist in co-regulating ATP with sodium.

Fe is also quite essential in the body. In the samples, it has the highest concentration for the sample labeled EP (eaten and medication) (276575±3157 mg/kg) and has the lowest value (0.87±0.19 mg/kg) for RG (for medication). The relatively high level of Fe obtained from the sample

EP in comparison with the Fe concentration in the other kaolin samples could be attributed to the source of that particular kaolin sample. It could be obtained from a source that contains very high iron content. A particular sample (PB, eaten by pregnant women) did not detect any Fe concentration. Some of the samples recorded Fe concentrations that were less than the RDA value for Fe which is 8 mg. Insufficient Fe concentration in the body will cause anemia whilst an excess of iron will cause iron overload disorder.

Titanium concentrations with a range of  $1826 \pm 414$  to  $6624 \pm 993.6$  mg/kg were also detected in the kaolin samples. Similarly, arsenic concentrations were detected in some of the samples with values of  $7.48 \pm 2.66$ ,  $17.44 \pm 2.53$ ,  $18.53 \pm 2.71$  and  $1.78 \pm 0.267$  mg/kg being recorded. Cobalt concentrations were also detected in most of the kaolin samples. Their concentrations ranged from  $0.27 \pm 0.041$  to  $28.67 \pm 2.83$  mg/kg. Cobalt is required in the synthesis of vitamin B<sub>12</sub>, but because bacteria are required to synthesize the vitamin, it is usually considered part of vitamin B<sub>12</sub> deficiency rather than its own dietary element deficiency. Excess cobalt in the human system could also cause cobalt poisoning.

Finally, scandium concentrations were also recorded in most of the samples. Values ranging from  $0.87 \pm 0.19$  to  $9.47 \pm 0.29$  mg/kg were recorded. This is an indication that there is some contamination of the kaolin before it reaches the final consumer either through preparation or storage.

### CONCLUSION

All the "hyire" samples chosen for this work contains five major elements as well as other elements essential to life. Some of these elements were detected in high concentrations; hence the "hyire" samples are safe for human consumption based on only the essential elements. But As (in FT, RT and PB), Ti (in RG, RT, PB, EP and PE), Co (in RG and EP), and Fe (EP) levels in the "hyire" samples in the study area were a little higher considering the fact that it is either eaten or used for medication. These high levels could be attributed to contamination introduced during the manufacturing process. Hence some remediation interventions should be put in place in order to reduce the levels of these elements in the finished product. It is also important for the sources of the additives to be investigated to clarify its purity level. Since the

product is patronized by many Ghanaians, modern industries could invest in the manufacture of this popular product. These industries could make the manufacturing process more refined with the use of modern methods (this could help eliminate some of the contamination that was obtained in the samples). The agencies responsible for regulating food and drugs are alerted to take careful look at the "hyire" on the Ghanaian market and provide regulatory requirements for their producers to ensure safe use of kaolin in Ghana.

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