Neutron Activation Analysis of Kaolin of the South Eastern States Nigeria

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/BJAST/2016/25418

Editor(s):
(1) Osiris Wanis Guirguis Saleh, Biophysics Department, Cairo University, Egypt.
(2) Singiresu S. Rao, Prof. at Department of Mechanical and Aerospace Engineering, University of Miami, Coral Gables, USA.

Reviewers:
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Complete Peer review History: http://sciencedomain.org/review-history/14964

Original Research Article

ABSTRACT

This work investigates the components of Kaolin (nzu) in the five South Eastern states of Nigerian and the possible health benefits by using Neutron Activation analysis. The results of the investigation show the concentration of eighteen elements. These elements are Mg, Al, Ti, V, Mn, Na, K, As, U, Sc, Cr, Fe, Co, Zn, Rb, Cs, Zn, Rb, Cs, Ba, and Th, that were analysed using NAA in Kaolin (Nzu) collected from five South East states of Nigeria. Among these, the major elements detected include Mg, Al, Ti, Na, K, and Fe. The remaining occurred at minor and trace levels. The results also show that Kaolin (nzu) is highly enriched in Al, Ti, K, and Fe with concentration levels ranging from 132300±794−188400±1507, 2642±682−12200±647, 2029±114−5913±136 and 7809±187−18400±258. The concentrations of most of these elements is far exceeds the daily dietary needs or permissible limits of man, and thus making them toxic unless taken in small dosages.

Keywords: Neutron; quality; element; mineral; Kaolinite.

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1. THEORETICAL INTRODUCTION

Kaolin is used in the manufacturing of fine porcelain in China while the impure parts are used in making pottery, stoneware, and bricks. Bulk of this mineral (Kaolin) is used in the paper industry as fillers. Its whiteness is explored in improving paper brightness and opacity. It is applied as white wares providing strength and plasticity in ceramic products [1]. It is used to improve the optical, mechanical and rheological properties of paints and it is also used in pharmaceuticals for the production of human and veterinary medicine for the treatment of indigestion problems. Kaolin (nzu) is also used as organic manure in farming, as an insecticides applied to crops to prevent insect destruction and to reduce sun scald on apple production. (Mokobia’s recent investigation reveals that using this geological material for luminescence has the possibility of dating [2].

The digestive pharmaceutical kaopectate was formulated using kaolinite as its main ingredient, to aid in suppressing diarrhoea and reducing toxic effects in the digestive system. Interestingly, scientists from Louisiana State University who analyzed Nigerian clays commonly sold for consumption in West African markets discovered that the composition of nzu have striking similarities to that of the clays used in medicinal kaopectate.

In Nigeria, clays were mined from a depth of 30 to 90 cm from the surface, then sun-dry and smoke the blocks. These processes transform them into a substance locally known as nzu, and then taking to the market for sale in the region. Medical men (herbalists) combine this clay with substances from plants in several ailment remedies. The ailments are usually associated with pregnancy, and few cases of stomach upset such as dysentery. Four hundred (400) to five hundred (500) tons of this medicinal clay are produced and sold each year, a testimony to their wide use. The presence of aluminium and magnesium has made kaolin to posse antacid properties and can be a therapeutic food for people suffering from gastric upsets or ulcers. Also, because of its covering properties, it has a bandaging role in gastro-enterology [3].

Neutron Activation Analysis is an analytical technique for qualitative and quantitative determination of elements in a material based on the production of radioactive nuclei from stable nuclei in the material which is subjected to irradiation with neutrons in a nuclear reactor or sometimes in other neutron sources. The sample can be measured by detecting the decay of these nuclei. Instrumental Neutron Activation Analysis (INAA) is used to determine the concentration of trace and major elements in a variety of samples. A sample is subjected to a neutron flux and radioactive nuclides are produced. As these radioactive nuclides decay, they emit gamma rays whose energies are characteristics of each nuclide. Comparison of the intensity of these gamma rays with those emitted by a standard value, permits quantitative measurement of the concentrations of the various nuclides.

To carry out NAA, the specimen is placed in a suitable irradiation facility and bombarded with neutrons. This creates artificial radioisotope of the elements present. Following the irradiation, the artificial radioisotopes decay via emission of particles & gamma rays that are characteristics of the element from which they are emitted. Nigeria Research Reactor-1 (NIRR-1) is an example of a nuclear reactor which was installed and commissioned at the Center for Energy Research and Training (CERT), Ahmadu Bello University Zaria, Nigeria. As a miniature Neutron Source Reactor (MNSR), it has a tank-in-pool structural configuration with a normal thermal power rating of 31 kW. NIRR-1 is acquired for an extensive soil fertility mapping project of the different arable lands in Nigeria aimed at improving food production. Like all MNSR facilities, NIRR-1 is specifically designed for NAA [4].

1.1 Quality Assurance of Analyzed Samples

Reference materials play a fundamental role in the quality assurance of measurements. In this regard, NIST 1633b Coal Fly Ash reference material was used for quality assurance of this work.

The precision and accuracy of the analytical technique (INAA) was assessed by simultaneous activation of reference material NIST-SRM 1633b Coal Fly Ash. Table 1 shows the analytical results obtained for Mg, Al, Ti, V, Mn, Na, K, As, Sm, U, Cr, Fe, Sc, Co, Zn, Rb, Cs, Ba, and Th at NIRR-1 laboratory for the reference material compared with the samples.
Table 1. Analytical results and recommended values of NIST-SRM 1633b coal fly ash certified reference material (Mg/kg)

| Element | Reported | This study |
|---------|----------|------------|
| Al      | 1655.5   | 154380     |
| Fe      | 855.8    | 48076      |
| Mg      | 53.02    | 8537       |
| Na      | 22.11    | 330        |
| Ti      | 87.01    | 2642       |
| K       | 214.5    | 2029       |
| As      | 136.2    | 5.0        |
| Ba      | 709      | 213        |
| Cr      | 198      | 155        |
| Mn      | 131.8    | 136.2      |
| Th      | 25.7     | 26.1       |
| U       | 8.79     | 4.0        |
| V       | 295.7    | 259        |
| Co      | 50       | 8.2        |
| Cs      | 11       | 5.1        |
| Sc      | 41       | 22.3       |
| Zn      | 210      | BDL        |
| Sm      | 20       | 14.45      |
| Rb      | 140      | BDL        |

2. METHODOLOGY

2.1 Sampling

Kaolin (nzu) samples were randomly collected from five (5) South-East States. The samples were stored in clean polyethylene bags before transportation to the laboratory.

2.2 Sample Preparation Using NAA

This consists primarily of weighing and packaging. Sample pretreatment which involves removal of impurities followed by grinding to finer particles using Agate mortar and pestle was carried out. Representative samples were thereafter collected from the pretreated samples. Test samples obtained this way, were again homogenized to finer particles. The samples were then sieved through stainless steel with an aperture of 75 microns. The samples were systematically labeled to reflect sample type and location. The agate mortar and pestle were washed, dried and cleaned with acetone and de-ionized water before a new sample was pulverized in order to avoid cross contamination of the samples. Approximately 0.2 g of the geological samples were weighed, packed into vials and sealed for subsequent irradiation with thermal neutrons.

2.3 Sample Irradiation

The analytical process involves both short and long irradiation with neutrons from the Miniature Neutron Source Reactor (NIRR-1) situated at the Centre for Energy Research and Training Zaria. In the case of short irradiation, the sample to be analyzed is enclosed in 7 cm³ rabbit capsules and sent for irradiation one after the other in one of the outer irradiation channels B. This has a neutron flux of 2.5 x 10¹¹ n/cm²s and the irradiation was timed for 600 seconds. In the case of long irradiation, several samples stacked inside the 7 cm³ rabbit capsule, were transferred to any of the smaller inner irradiation channels A, B1, B2 and B3 with a neutron flux of 5 x 10¹¹ n/cm²s using the pneumatic transfer system. In order to limit neutron flux corrections during sample analysis, the neutron flux reaching the samples were kept constant. This was observed on the micro-computer connected to the neutron chamber in the inner irradiation channel. After irradiation, the samples were retrieved via the pneumatic transfer and kept in a glass chamber.

2.4 Spectral Acquisition

The PC-based gamma-ray spectrometry set-up performs measurement of induced radioactivity in the various samples analyzed. After, the short irradiation protocol, a waiting period of 2 to 15 minutes was allowed before the first counting regime which lasted 10 minutes was carried out. The sample to be counted was placed on a plexiglass spacer to maintain source-detector geometry of 5 cm. This counting regime is depicted S1. The second counting regime was carried out between 3-4 hours after the first counting was also carried out for 10 minutes using a plexiglass spacer depicted H1 corresponding to sample-detector geometry of 1 cm. In the case of long irradiation, the first counting regime depicted as L1 was carried out after a waiting period of 4 – 5 days for duration of 30 minutes using sample –detector geometry of 1 cm. The second counting regime was carried out after a cooling period of 10-15 days for duration of 60 minutes. This is depicted as L2 and samples-detector geometry of 1 cm was also used. Table 2 shows the irradiation and counting scheme used for sample analysis.
Table 2. Sample irradiation and counting scheme

| Type of Irradiation | Waiting period         | Count duration | Plexi-glass sample holder | Source detector geometry (cm) |
|---------------------|------------------------|----------------|---------------------------|-------------------------------|
| Short-1st lap (S1)  | 12-15 min              | 10             | H₂                        | 5                            |
| Short-2nd lap (S2)  | 3-4hrs after 1st count | 10             | H₁                        | 1                            |
| Long-1st lap (L1)   | 4-5 days               | 3              | H₁                        | 1                            |
| Long-2nd lap (L2)   | 10-15 days             | 60             | H₁                        | 1                            |

3. RESULTS AND DISCUSSION

Table 3 shows the concentration of eighteen elements. These include Mg, Al, Ti, V, Mn, Na, K, As, U, Sc, Cr, Fe, Co, Zn, Rb, Cs, Zn, Rb, Cs, Ba, and Th. The samples were analysed using NAA in Kaolin (nzu) collected from five South East states of Nigeria. Among these, the major elements detected include Mg, Al, Ti, Na, K, and Fe. The remaining occurred at minor quantity and trace levels. Table 3 shows that Kaolin (Nzu) is highly enriched by Al, Ti, K, and Fe with concentration levels ranging from 132300±794–188400±1507, 2642±682–12200±647, 2029±114–5913±136 and 7809±187–18400±258. Each major mineral is required in several hundred milligrams daily while the trace/minor minerals are required in few milligrams daily [5]. The results obtained, compared favourably well with the recommended values from the quality assurance.

The levels of Mg in the Kaolin samples were at the highest and at the lowest in Anambra and Ebonyi states respectively. Magnesium, Mg, was not detected in Enugu state. However, the values obtained for all the samples were higher than the Recommended Dietary Allowance (RDA) of 420mg [6]. Magnesium is required for energy production, oxidative phosphorylation and glycolysis. It contributes to the structural development of bone and is also required for the synthesis of DNA, RNA and antioxidant glutathione. The high levels of Mg are desirable as it is needed in the secretion of several enzymes [7].

Aluminium levels range from 132300 mg/kg in Abia to 188400 mg/kg in Anambra. The levels of
Al in all the states are relatively high; this is attributed to the fact that Al is the main composition in kaolin and is also one of the most abundant metals in earth crust. However, intake of large amount of Al can cause anemia, osteomalacia (brittle or soft bones), glucose intolerance and cardiac arrest in Humans.

Titanium is the ninth most abundant metal in the earth crust. Titanium concentration in the range of 2642 mg/kg to 12200 mg/kg was detected in the kaolin sample. Studies show that titanium causes adverse effects by producing oxidative stress, resulting in cell damage, redness, and immune response [8].

Table 3. Elemental concentration (mg/kg) of Kaolin samples from five South-East states of Nigeria

| Element | Ebonyi | Imo | Abia | Enugu | Anambra |
|---------|--------|-----|------|-------|---------|
| Mg      | 3200±922 | 3459±1062 | 3504±820 | BDL | 4917±939 |
| Al      | 167400±1674 | 143200±1146 | 132300±794 | 140600±1824 | 188400±1507 |
| Ti      | 12200±647 | 2642±682 | 12010±577 | 10190±866 | 12130±667 |
| V       | 114±9 | 180±6 | 234±6 | 259±10 | 139±9 |
| Mn      | 136.20±1.2 | 15±0.5 | 29±1 | 21±1 | 30±1 |
| Na      | 330±2 | 6037±18 | 716±3 | 7125±21 | 519±3 |
| K       | 5913±136 | 3305±446 | 2029±114 | 2596±459 | 2377±116 |
| As      | 3.15±0.14 | 2.60±0.3 | 4.70±2 | 5.00±0.3 | 2.90±0.2 |
| Sm      | 10.44±0.03 | 14.45±0.04 | 10.67±0.03 | 12.63±0.04 | 13.39±0.04 |
| U       | 3.40±0.2 | 3.10±3 | 4.00±0.3 | 3.10±0.3 | 3.40±0.3 |
| Sc      | 22.3±0.1 | 15.45±0.09 | 13.45±0.08 | 14.42±0.09 | 18.64±0.09 |
| Cr      | 123±3 | 155±4 | 140±3 | 133±4 | 151±4 |
| Fe      | 18400±258 | 8537±213 | 7809±187 | 10260±215 | 15350±261 |
| Co      | 8.20±0.3 | 2.20±0.3 | 2.20±0.3 | 2.50±0.2 | 3.70±0.3 |
| Zn      | 37±6 | 55±6 | BDL | BDL | BDL |
| Rb      | 54±5 | 26±4 | BDL | BDL | BDL |
| Cs      | 5.10±0.4 | 3.60±0.4 | 1.70±0.3 | 1.90±0.3 | 2.20±0.6 |
| Ba      | 213±31 | 205±36 | 173±36 | 161±30 | 129±33 |
| Th      | 23.90±0.3 | 21.50±0.3 | 24.80±0.3 | 21.90±0.3 | 26.10±3 |

**BDL** : Below Detection Limit

Fig. 2. Distribution of elements found in Kaolin samples of five South-East States
Generally, the levels of Vanadium in the kaolin samples were relatively low as compared to other elements. Enugu has the highest level of V with 259 mg/kg and lowest in Ebonyi with 114 mg/kg. In a related study [7], gave the mean concentration of vanadium in the kaolin sample as 127.71 mg/kg. This element appears not to be utilized by humans.

Manganese is an essential element that is normally stored in the kidney and liver in the body. Its presence in the body maintains normal bone structure, reproduction and normal functioning of the Central Nervous System. It is also required for various biochemical and enzymatic processes and helps in eliminating fatigue. The Mn levels range from 15 mg/kg to 136.2 mg/kg. The RDA for Mn is 2 mg/day. From this analysis, it is observed that the Mn concentrations obtained in these samples are far above this value. Though, Mn is a co-factor in enzyme functions, excess of it could cause manganism [7].
Table 4. Recommended Dietary Allowances (RDA) of some elements for pregnant and lactating women (DRI, 2001)

| Element     | Pregnant | Lactation |
|-------------|----------|-----------|
| Calcium (mg/d) | 1000    | 1000      |
| Chromium (mg/d) | 0.03    | 0.045     |
| Copper (µg/d) | 1000    | 1300      |
| Iron (mg/d)  | 27      | 9         |
| Manganese (mg/d) | 2      | 2.6       |
| Zinc (mg/d)  | 11      | 12        |
| Potassium (mg/d) | 4700  | 5100      |
| Sodium (mg/d) | 1500   | 1500      |
| Cobalt (µg/d) | 0.006  |           |
| Magnesium (mg/d) | 420  | 420       |

Sodium levels also ranged from 330 mg/kg in Ebonyi to 6037 mg/kg in Imo. The RDA of sodium is 1500mg; it is a systemic electrolyte and is essential in co-regulating ATP with potassium [9].

Potassium exists as an intercellular constituent in the body. The level of Potassium in this study ranges approximately between 2029 mg/kg in Abia to 5913 mg/kg in Ebonyi. This is an indication that the intake of kaolin (nzu) can therefore serve as a good source of potassium.

Similarly, Arsenic concentrations were detected in all the samples with values of 3.15 mg/kg, 2.6 mg/kg, 4.7 mg/kg, 5 mg/kg and 2.9 mg/kg. In a study carried out by [10], he gave the mean intake of arsenic by adult men and women to be approximately 2.0 to 2.9 µg/day and 1.7 to 2.1 µg/day. Also ingestion of doses greater than 10mg/kg/day leads to encephalomy and gastrointestinal symptoms such as nausea, diarrhea and abdominal pain [11]. It is an essential element for living organisms. Its presence in the body is associated with transfer of oxygen from lungs to tissue cells and to hemoglobin in the blood cells. It has its lowest concentration in Imo (8537 mg/kg) and highest concentration in Ebonyi (18400 mg/kg). The relatively high level of Fe obtained from the samples could be attributed to the source of the kaolin sample; it could be obtained from a source that contains very high iron content. The RDA value for Fe is 27 mg/day for pregnant women and 9 mg/day for lactating women. Insufficient concentration of Fe in the body which is mainly caused by poor dietary intake results in anemia and excessive menstrual flow [12], while excess of it could lead to chronic overload of Fe in the body.

Cobalt concentrations ranged from 2.2 mg/kg to 8.2 mg/kg. Cobalt is required in the synthesis of vitamin B₁₂, but because bacteria are required to synthesize the vitamin, it is usually considered part of vitamin B₁₂ deficiency rather than its own dietary deficiency. Excess cobalt in the human system could also cause cobalt poisoning.

Zinc is among the nutritional important elements [13]. It is a constituent of many enzymes and
insulin. Zinc is necessary for the growth and multiplication of skin cells, bone metabolism and functioning of taste and eyesight [14]. Zinc deficiency is characterized by recurrent infections, lack of immunity, growth retardation, skin change and poor appetite. Pregnant and lactating women require 11 to 12 mg/day [6].

Zinc concentration in the kaolin samples were only recorded in Imo and Abia states with a concentration range of 37 – 55 mg/kg respectively. Estimated safe and adequate daily intake of Zn is between 10 and 20 mg/day [15]. Moreover, prolonged consumption of large doses can result in some health complications such as fatigue and dizziness [16].

Uranium concentration ranges from 3.1 g/kg in Imo and Enugu to 4 mg/kg in Abia. In a related study carried out by [17], the uranium concentration in the kaolin sample was (1.2 – 4.1 mg/kg). The average daily intake of uranium ranges from 0.07 – 1.1 µg/day. The intakes of uranium exceeding EPA standards can lead to increased cancer risk, liver damage or both [17].

Thorium concentration in the Kaolin sample across the states shows Anambra having the highest concentration with 26.1 mg/kg, Abia 24.8 mg/kg, Ebonyi 23.9 mg/kg, Enugu 21.9 mg/kg and Imo 21.5 mg/kg. Chromium is a metal which is also called “an essential trace element” because very small amount of it is necessary for human health. Chromium concentration was detected in all the kaolin samples across the states. They range from 123 mg/kg in Ebonyi to 155 mg/kg in Imo state. The US National Research specifies an Estimated Safe and Adequate Daily Dietary Intake (ESADDI) of 0.05 – 0.2 mg/day for adults and 0.01 – 0.04 mg/day for children (0-5 years). Chromium is used for improving blood sugar control for people with diabetes; it is also used to improve depression, weight loss, and athletic performance. However, long periods of use can lead to some negative side effects such as skin irritation, headaches, dizziness, nausea, mood changes and impaired thinking.

Finally, scandium concentrations were also recorded in most of the samples, values ranging from 13.45 mg/kg to 22.3 mg/kg.

4. CONCLUSION

The levels of Mg in the Kaolin samples were highest in Anambra state and lowest in Ebonyi state. Magnesium, Mg was not detected in Enugu state. However, the values obtained for all the samples were higher than the Recommended Dietary Allowance (RDA) of 420 mg [6]. Magnesium is required for energy production, oxidative phosphorylation and glycolysis. It contributes to the structural development of bone and is also required for the synthesis of DNA, RNA and antioxidant glutathione. The high levels of Mg are desirable as it is needed in the secretion of several enzymes [7]. Based on this study, the south-east kaolin (nzu) is characterized with exceptionally high concentration of Fe, K, Al, and Mg. This implies that geophagic individuals consuming these clays may benefit from their possible medicinal and nutritional values. However, some elements were also present in high concentration far above the daily dietary need of man; hence continuous consumption of this clay can result to bioaccumulation of these elements and hence, can pose serious health hazard to its consumers.

COMPETING INTERESTS
Authors have declared that no competing interests exist.

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