



X-RAY DIFFRACTION ANALYSIS IN TEXTURAL STUDIES OF SOME SOIL MINERALS IDENTIFIED IN RIVERS STATE OF NIGERIA

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ABSTRACT

The X-ray diffraction analysis of some soil identified in Rivers State of Nigeria, Sodium Aluminum Silicate and Potassium Aluminum Silicate ($NaAlSi_2O_6$ and $KAlSi_2O_6$) were studied using the Debye-Scherrer method and a diffractometer. The lattice constants were evaluated using CuK_{α} radiation of wavelength, $\lambda = 1.5418 \text{ \AA}$ and the results obtained were $13.730 \pm 0.006 \text{ \AA}$ and $13.500 \pm 0.006 \text{ \AA}$ for $NaAlSi_2O_6$ and $KAlSi_2O_6$ respectively. The sizes of the unit cell were examined in terms of textural parameters such as particle size and number of atoms per unit cell. The values of the lattice constants suggest their Bravis lattice, the metal to metal distances, the metal to non-metal distances and the distance of closest approach of the atom centres. The metal to metal and non-metal to non-metal distances were obtained as $9.71 \pm 0.002 \text{ \AA}$ and $4.278 \pm 0.002 \text{ \AA}$ respectively for Sodium Aluminum Silicate; while it's metal to non-metal distance was obtained as $5.160 \pm 0.002 \text{ \AA}$. Also metal to metal and non-metal to non-metal distances were obtained as $9.55 \pm 0.002 \text{ \AA}$ and $4.440 \pm 0.002 \text{ \AA}$ respectively for Potassium Aluminum Silicate; and it's metal to non-metal distance was obtained as $5.760 \pm 0.002 \text{ \AA}$.

Keywords: Lattice constants, Bravis lattice, Diffractometer, Cells, Particle size, Textural parameters

INTRODUCTION

In recent years, it has been shown by various researchers that X-ray diffraction technique can be used to obtain valuable information about crystalline systems. It began with the experimental difficulty in establishing the wave nature of X-rays by [Roentgen \(1895\)](#) through a direct measurement of X-ray wavelength. [Brag \(1947\)](#) determined the structure of potassium chloride, sodium chloride and magnesium chloride using X-ray diffraction technique. [Dent \(1977\)](#) reported the diffraction patterns of powder crystalline particles such as Lithium Fluoride. [Jefferson \(1978\)](#) obtained the lattice constants for two structural variants of ganophyllite (the monoclinic and triclinic systems) which is a Manganese Aluminium silicate. [Opuwaribo and Odu \(1978\)](#) have reported on the Ammonia fixation on some Nigerian soils. [Aladekomo and Bragg \(1990\)](#) found the structural transformations induced in graphite by grinding, using X-ray diffraction line profiles.

Textural studies on crystalline systems generally employ a material in which there are many microscopic crystals oriented at random in all directions. This method greatly extended the range of crystalline matter which can be analysed, because of their technological importance. Hence microcrystals of some clay fractions of tropical soil such as $NaAlSi_2O_6$ and $KAlSi_2O_6$ have undergone some investigations in the last few years because of their interesting physical properties which are of great technological and agricultural importance. [Hastings and Corliss \(1970\)](#), reported some textural properties such as the magnetic properties of NiS_2 , where they found two transition temperatures ($TNi_1 \cong 31K$ and $TNi_2 \cong 45K$). [Hughes and Brown \(2005\)](#) have studied the effect of non-stoichiometry on the electrical and magnetic properties of NiS_2 and also made experimental investigations of the magnetic properties of CuS_2 . [Wilson \(1969\)](#) and [Prokhatilov and Isakina \(1980\)](#), found the X-ray powder diffraction intensity of Sodium Chloride (NaCl) by setting the diffractometer counter mean $2\theta=0$. [McKenzie et al. \(2002\)](#), studied soil physical measurement and interpretation for land evaluation. Most investigators focused considerable attention on the magnetic, electric and optical properties, and have thrown little light on the textural properties. While only the shape and size of the unit cell of these crystal structures have been determined, more light will be thrown on the grain size, orientation with reference to diffraction pattern, phase and number of atoms per unit cell of these tropical clay soil minerals. The industrial importance for determining these textural parameters lies in the influence often very important which they have on the overall microscopic and macroscopic properties. Thus an X-ray diffraction analysis in textural studies of these polycrystalline specimens shows the Debye rings whose crystalline having the reflecting planes almost parallel to the specimen surface contribute to certain reflection. Furthermore, the studies highlight the extent to which the low and high clay minerals can be indexed with high precision.

Experimental Techniques

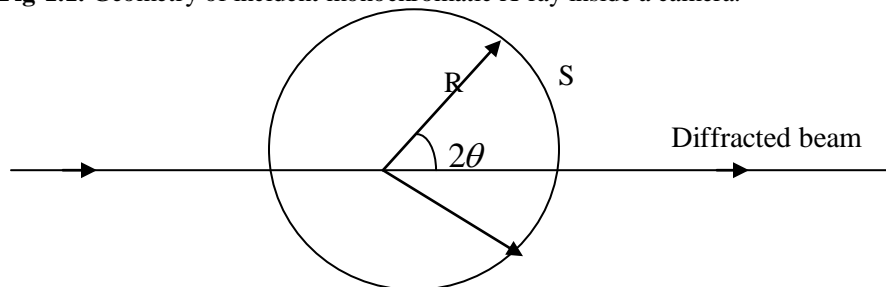
Hull (1917) was one of those that devised the powder method of X-ray diffraction. It is the most generally useful of all diffraction methods especially in textural studies of polycrystalline substances. Basically, this method involves the diffraction of monochromatic (strong $K\alpha$) characteristic component of the filtered radiation from an X-ray tube of Cu target operated at about 50KV, 20mA. The use of this technique is suitable in the study of textural properties of powder samples of clay soil fractions such as $NaAlSi_3O_8$ and $KAlSi_3O_8$ because of their micro-crystalline nature at its non-destructive state. Opara (1994) used this method in studying the monocrystalline substances and also, Omubo-Pepple and Opara (2005) studied the electrical properties of molten pyrite crystals using the same method.

METHOD

Filings of the specimens were made into a paste using a very thin transparent celotape at 32°C and placed at the centre of the power camera. The powder specimens were numerous placed at random so that all planes have a chance to reflect in all possible orientations giving lines that are continuous. Two reference samples, copper and tungsten and the samples of the tropical clay soils were used. The reference metals were supplied by Riedel-de Haen Aktiengesellschaft Wunstorfer in Germany, while clay fractions were prepared using the method of Opara (2004). The powder samples were stored in desiccators over a drierite when not in use. X-ray diffraction measurements were made with an upgraded and modified diffractometer with camera (solid state, Teltron, London), and proportional counter. The Debye camera used consisted essentially of a black plastic cylindrical chamber with a light black plastic cover with a collimator to admit and define the incident monochromatic X-ray beam. A beam stop to confine and stop the transmitted beam, a means for holding the film tightly against the inside circumference and a rotatable specimen holder were provided in the camera use. The distance measured on the film from a particular diffraction line to the point where the transmitted beam could strike the film is S , and its relationship with the glancing angle θ and the radius of the camera R (Fig. 1.1) can be written as:

$$S = R 2\theta \quad (1)$$

Fig-1.1. Geometry of incident monochromatic X-ray inside a camera.



If we consider two sets of planes of very nearly the same spacing, it will give rise to two diffracted beams separated by a small angle $\Delta 2\theta$. The separation of the lines on the film will be

$$\Delta S = R\Delta 2\theta \quad (2)$$

The resolving power which is the ability of the camera to separate diffraction lines from sets of planes very nearly the same spacing can be found by differentiating the Bragg law:

$$n\lambda = 2d \sin \theta \quad (3)$$

That is
$$\frac{d\theta}{d\lambda} = \frac{1}{\lambda} \tan \theta \quad (4)$$

From eqn. (2)
$$\frac{d\theta}{dS} = \frac{1}{2R} \quad (5)$$

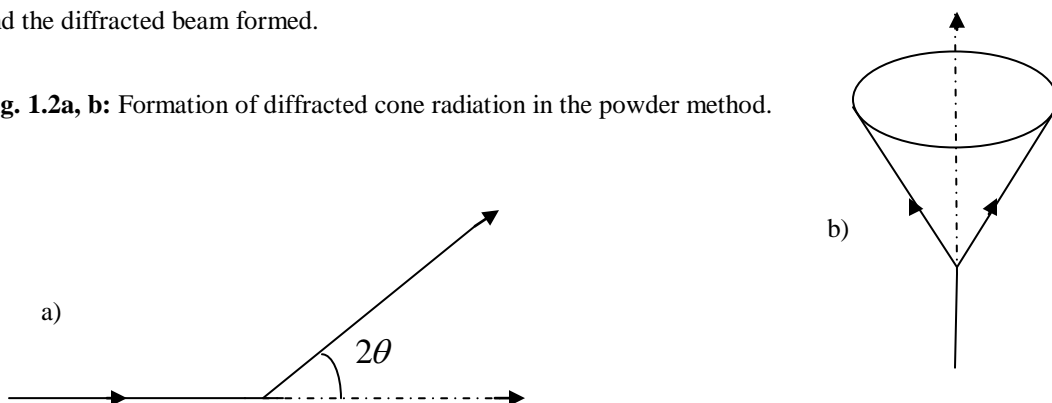
Therefore, resolving power
$$\frac{D}{\Delta\alpha} = \frac{2R}{s} \tan \theta \quad (6)$$

Where D is used to depict differentials, $\Delta\alpha$ is the difference in their spacing, and ΔS is the separation of two diffraction lines which appear resolved on the X-ray film.

Specimen Preparation and Film Loading

The final specimen for the Debye-camera is in the form of a thin rod of size 0.45mm thick and about 1.2cm long. This was prepared by coating the powder specimen on the gummy surface of transparent cello tape. It was then folded into a cylindrical shape and mounted in a holder so that it lay accurately along the rotation axis of the camera. Since each particle of the specimen under examination was a tiny crystal or assemblage of smaller crystals, oriented at random with respect to the incident beam, it was by chance that some of the crystallites were correctly oriented, so that their diffraction planes for example could reflect the incident beam. The result was that every set of lattice planes were capable of reflection. The mass of this powder sample was in fact, equivalent to a single crystal rotated, not about one axis but about all possible axes. Considering one particular one particular hkl reflection, one or more crystals would by chance, be oriented such that their (hkl) planes make the correct Bragg angle for reflection. Figure 1.2a shows one plane in this set and the diffracted beam formed.

Fig. 1.2a, b: Formation of diffracted cone radiation in the powder method.



When this plane rotated about the incident beam as axis in such a way that θ was kept constant, the reflected beam would travel over the surface of a cone as shown in Figure 1.2b, the axis of the

cone coinciding with the transmitted beam. However, the powder samples were not rotated, since the presence of a large number of crystallites have all possible orientations and are equivalent to rotation. Hence, among these particles there would be a certain fraction whose (hkl) planes make the right Bragg angle with the incident beam and at the same time lie in all possible rotational positions about the axis of the incident beam. The hkl reflections from these samples had the form of a conical sheet of diffracted radiation and a separate cone was formed for each set of differently spaced lattice planes as shown in Figure 1.2a, b.

A 35mm film was cut to the required width and length and fixed inside the cylindrical camera in the darkroom. When the film WAS laid out flat, a hole was punched in the centre of the film, and the θ value of a particular reflection obtained by measuring $2s$ (the distance apart of two diffraction lines formed by the same cone of radiation with the relation from equation (1). The unsymmetrical film loading technique used during standardization had holes punched in the film so that it may be slipped over both the entrance collimator and the beam top. This loading technique was preferable because it provided for film correction without calibration of the camera.

Recording Diffracted Radiation

One of the most efficient and accurate way of interpreting X-ray diffraction patterns of powder specimen is to use an electronic digital detector (model AVD890C). The intensity of the diffracted beam was measured directly by the electronic counter, which converted all incoming X-rays into pulses of electric current in the circuit connected to the counter. The counter counted the number of pulses while the timer recorded the time for such pulses, hence the intensity was recorded in counts/sec or pulses/sec, since intensity was proportional to the number of counts per unit time. The counter was set at $2\theta=0$ and connected to a count rate meter, the output of which was fed to a strip-chart recorder. The counter was then moved through increasing values of 2θ until the whole angular range was "scanned". The paper chart on the recorder moved corresponding angles 2θ , such that the distance along the length of the chart was proportional to 2θ . The results of the lattice constants are given for samples of copper, tungsten, $\text{NaAlSi}_2\text{O}_6$ and KAlSi_2O_6 (Tables 1-4). The arrival of X-ray quanta in the counter was random in time, and the accuracy of the counting rate measurement was governed by the laws of probability:

$$\text{Relative Standard Deviation} = \frac{100}{\sqrt{N}} \% \quad (7)$$

$$\text{While possible error} = \frac{67}{\sqrt{N}} \% \quad (8)$$

A statistical counting error \mathcal{E} was also calculated from the equation

$$\varepsilon \% = \frac{100}{\sqrt{T}} - \frac{1}{\sqrt{R_p - R_b}} \quad (9)$$

Where R_p is the peak count rate, R_b is the background count rate and T is the total analysis time.

The $\varepsilon\%$ was then calculated for the gas counter in use, for a fixed analysis time T that is taken as figure of merit to be 39.50. However, corrections were made on the effect of dead time of the detector in use. In this work, the true count rate R_T was found using the equation;

$$R_T = \frac{R_m}{1 - R_m \alpha_k} \quad (10)$$

Where R_m is the measured count rate and α_k is the dead time in microseconds of the detector. The two values of the wavelength of monochromatic X-ray were noticeable from the diffractogram. The wavelength of the CuK_α lines were $CuK_{\alpha_1} = 1.5405 \text{ \AA}$ and $CuK_{\alpha_2} = 1.5443 \text{ \AA}$. Thus the angular separation of the CuK_{α_1} and CuK_{α_2} doublet was found as function of the angle 2θ . The separation was found using

$$d\theta = \frac{d\lambda}{\lambda} \tan \theta \quad (11)$$

Substituting the given values of $d\lambda = 0.0038 \text{ \AA}$ and $\lambda = 1.5418 \text{ \AA}$, we get

$$d\theta = 0.002 \times 57.3 \tan \theta$$

RESULTS AND DISCUSSIONS

The textural properties of these substances such as shape, grain size, etc., determine the angular positions of the diffracted lines and consequently determine the diffraction pattern of the substances, Opara (1994). The shape and size of the unit cell were deduced from the angular positions of the diffracted lines. This was done by indexing the pattern with the correct choice of crystal system. Hence, the shape of the unit cell was known from the crystal system and its size calculated from the position and Miller indices of the diffraction lines.

The X-ray powder patterns of the samples were obtained using CuK_α radiation ($\lambda_{CuK_\alpha} = 1.5418 \text{ \AA}$). The Bragg angles 22.5° , 25.5° , 37.5° and 20° , 29° , 36.4° for the standard samples of copper and tungsten were respectively obtained and are shown in Tables 1 and 2. Using the equation

$$\frac{\sin^2 \theta}{N} = \left(\frac{\lambda}{2a} \right)^2 (h^2 + k^2 + l^2) \quad (12)$$

the lattice constants were calculated from each line position. The mean lattice constants $3.57 \pm 0.006\text{\AA}$ and $3.173 \pm 0.002\text{\AA}$ for copper and tungsten respectively were calculated within the limits of experimental errors. From the International Table on Crystallography, the analysis of the line positions leads to the conclusion that the substances are copper and tungsten respectively. From the X-ray Crystallographic Data book, the lattice constant for copper of *fcc* (face-centered cubic) structure was given as 3.6148\AA at 25°C , while for tungsten of *bcc* (body-centre cubic) lattice was given as 3.1653\AA at 25°C . These results were in general agreement with the results obtained as standards in this work within the limits of experimental error.

Table-1. Lattice constant for copper powder (Standard sample 1)

Line	θ	$\text{Sin}^2\theta$	$N=h^2+k^2+l^2$	$\frac{\text{Sin}^2\theta}{N}$	$a\text{\AA}$	<i>hkl</i>	$d\theta$
1	22.5°	0.1460	3	0.0488	3.49	111	0.05850
2	25.5°	0.1853	4	0.0463	3.57	200	0.06674
3	37.5°	0.3705	8	0.0463	3.57	220	0.10840

Table-2. Lattice constant for tungsten powder (Standard sample 2)

Line	θ	$\text{Sin}^2\theta$	$N=h^2+k^2+l^2$	$\frac{\text{Sin}^2\theta}{N}$	$a\text{\AA}$	<i>hkl</i>	$d\theta$
1	20.06°	0.1176	2	0.0588	3.175	110	0.05140
2	29.06°	0.2259	4	0.0589	3.170	200	0.07830
3	36.43°	0.3526	6	0.0588	3.176	211	0.10410

The results of the X-ray powder diffraction pattern of the tropical clay soil minerals, $\text{NaAlSi}_2\text{O}_6$

and KAlSi_2O_6 are shown in Tables 3 and 4.

Table-3. Lattice constant for Sodium Aluminum Silicate powder (Sample 3).

Line	θ	$\text{Sin}^2\theta$	$N=h^2+k^2+l^2$	$\frac{\text{Sin}^2\theta}{N}$	$a\text{\AA}$	<i>hkl</i>	$d\theta$
1	4.53°	0.0062930	2	0.00314650	13.74	110	0.0112
2	6.45°	0.0126194	4	0.00315485	13.73	200	0.0160
3	7.90°	0.0188910	6	0.00314850	13.73	211	0.0196
4	9.14°	0.0252324	8	0.00315400	13.73	220	0.0227
5	10.23°	0.0315417	10	0.00315410	13.73	221	0.0255

Table-4. Lattice constant for Potassium Aluminum Silicate powder (Sample 4).

Line	θ	$\text{Sin}^2\theta$	$N=h^2+k^2+l^2$	$\frac{\text{Sin}^2\theta}{N}$	$a \text{ \AA}$	hkl	$d\theta$
1	3.274°	0.0032616	1	0.0032616	13.50	100	0.0807
2	4.630°	0.0065158	2	0.0032597	13.50	110	0.0114
3	5.680°	0.0097955	3	0.0032618	13.50	111	0.0140
4	6.550°	0.0130120	4	0.0032530	13.51	200	0.0162
5	7.360°	0.0164104	5	0.0032808	13.50	210	0.0182

The glancing angles for $\text{NaAlSi}_2\text{O}_6$ and KAlSi_2O_6 were found to vary from 4.55° to 10.23° and from 3.27° to 7.36° for the first and last rings respectively as observed on the X-ray photograph when laid on a smooth surface at a temperature of about 30°. The space structure of this clay mineral was found to be cubic which compared favourably with the earlier result obtained by [Opara and Gholap \(1988\)](#). The Bravais lattice for $\text{NaAlSi}_2\text{O}_6$ was found to be of body-centered cubic (*bcc*) lattice system with distance of closest approach of the atomic centres in the crystal calculated as:

$$D_c = \frac{\sqrt{3}}{2} x a = \frac{\sqrt{3}}{2} x 13.73 = 11.890 \pm 0.002 \text{ \AA}$$

The metal to metal distance is $D_{M-M} = \frac{13.73}{\sqrt{2}} = 9.71 \pm 0.002 \text{ \AA}$, the non-metal to non-metal distance, $D_s = a(1-2\alpha)\sqrt{3} = 13.73(1-2 \times 0.405)\sqrt{3} = 4.278 \pm 0.002 \text{ \AA}$, while the metal to non-metal distance, $D_\lambda = a(3\alpha^2 - 2\alpha + 0.5)^{1/2} = 5.160 \pm 0.002 \text{ \AA}$.

The lattice constant for KAlSi_2O_6 was found to be $13.50 \pm 0.002 \text{ \AA}$ with sequence diffraction lines found to be of simple-centered cubic (*scc*). For simple-centered cubic lattices, the distance of closest approach D_c is equal to the value of the lattice constant. The metal to metal distance is

$$D_{M-M} = \frac{13.50}{\sqrt{2}} = 9.55 \pm 0.002 \text{ \AA}$$

The non-metal to non-metal distance,

$$D_{\delta} = a(1 - 2\alpha)\sqrt{3} = 13.50(1 - 2 \times 0.405)\sqrt{3} = 4.440 \pm 0.002 \text{ \AA},$$

while the metal to non-metal distance, $D_{\lambda} = a(3\alpha^2 - 2\alpha + 0.5)^{1/2} = 5.760 \pm 0.002 \text{ \AA}.$

The results of the distance of closest approach D_c , the metal to metal distance D_{M-M} and the non-metal to non-metal distance D_{δ} for the clay minerals show that the layer of spheres may be arranged in a single simple packed layer by placing each sphere in contact with each other. This type or arrangement depicts the simple crystal structure of these clay minerals, which are given in terms of the cubic cell.

CONCLUSION

In this investigation, we have outlined the determination of the lattice constants of the samples by studying the positions of the diffracted beams, with the object of determining the size and shape of the unit cell. The lattice parameters, the distance of closest approach of atom centres in the crystal, D_{M-M} , D_{M-S} and D_{M-N} in addition to the particle size, gave us certain ideas about the relative sizes of atoms which is independent on the kind of structure at room temperature. In these investigations we assumed that our samples show no symptoms of disorder or twinning.

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