

MINERAL CHARACTERIZATION OF YOMBO-FITTA - AN AFRICAN NATURAL HAIR DYE.***Adebayo, G. B, Adekola, F. A ^a and Olatunji, G. A**

Chemistry Department, University of Ilorin, Ilorin, Nigeria.

* Author for Correspondence

E-mail. adebayochem@yahoo.com.**Abstract**

Mineral contents of an African hair dye were investigated. Some physicochemical properties such as solubility, pH, ash and organic content were first carried out. Combinations of XRF, XRD, SEM, IR, and UV-VISIBLE spectroscopic techniques were employed in the investigation. The dye was found to dissolve in all the ten aqueous and non-aqueous media used. The pH of the aqueous solution was found to be 8.6. Ash and organic contents of the raw dye were found to be 51% and 49% respectively. The XRF revealed that the dye contains twenty elements which include K, Ca, Ti, V, Cr, Zn, Mn, Fe, Co, Ni, Cu, As, Nb, Zr, Rb, Sr, Y, Mo and Br, with concentrations ranging from major to ultra-trace levels. The XRD also showed that the sample contains about forty six mineral phases which include both inorganic and organic components. The optical microscopic investigation gave indication that the dye was likely to be of the marine origin. The infrared (IR) measurements indicated that the sample contained functional groups such as C=O, C=C, C-C, C≡N, aromatic ring and metal-carbon chelate rings. The UV-VIS spectra show that the dye absorbed in the visible region with λ_{max} of the aqueous solution being 464.0 nm.

Introduction

Dyes are coloured substances which impart more or less permanent colour to other materials. There are two types of dyes; natural and synthetic dyes. Natural dyes include those from plant, animal and mineral sources. Mineral dyes come from ocher (yellow, brown, red) limestone or lime (white), manganese (black), cinnabar and lead oxide (red), azurite and lapis lazuli (blue), and malachite (green)[1]. Natural dyes may also be organic or inorganic in nature and are broadly classified into dyes and pigments [2, 3]. Dyes and pigments are

essentially different in their degree of solubilisation. Dyes are soluble intensely-

coloured substances that are applied in solution to the substrate, while pigments are insoluble colouring substances usually applied to a substrate in conjunction with some binding agents [4, 5]. Dyes and pigments of natural origin are now used mostly for small- scale textile handicraft [5,6].

The dye under investigation has been used in Nigeria for a long time with little or no research documentation on it. It is rock – like in nature just like the usual solid

minerals, but its major use is for dyeing hair. The aim of this work is to characterize the dye to provide information for its other potential uses.

Materials and Methods

Source of the Dye

The white rock-like mineral dye (*Yombo-fitta-Ghanian language*) was obtained from Emir's market in Ilorin, Nigeria. The original source of the dye according to the marketer was southern part of Ghana. For the purpose of this study the sample will be designated as YF.

Solubility Test

Solubility of the dye was investigated in fourteen (14) different solvents. The reagents/solvents include deionised water, hydrogen peroxide, acetone, benzaldehyde, acetaldehyde, ethanol, petroleum ether, concentrated trioxonitrate (V) HNO_3 , concentrated hydrochloric acid (HCl), methanol, diethyl ether, ethyl acetate, acetic acid and aniline. The test was carried out by adding 10mg of the well ground ($< 80 \mu\text{m}$) dye to 5 cm^3 of each of the above solvent in a test-tube at room temperature [7].

XRF Elemental Analysis of the Dye

The sample was also analyzed for trace elements using Energy Dispersive X-ray fluorescence (EDXRF) spectrometry at the Center for Energy Research and Training, Ahmadu Bello University, Zaria Nigeria. The sample preparation prior to elemental analysis consisted of crushing and grinding in a Tungsten Carbide Spex Mill followed by other procedures specific for the method of analysis [8]. The EDXRF facility consists of two interchangeable (55Fe and 109Cd) annular source, a Canberra model SL 12170 silicon solid state detector and the associated pulse processing electronic

device which are coupled to ADC-Card. The facility runs on PC with Maestro software for spectra acquisition. Sensitivity calibration using thick pure metal foils (Ti, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Sn, Ta, Pb) and stable analytical grade chemical compound K_2CO_3 , $CaCO_3$, Ce_2O_3 , WO_3 , ThO_2 and U_3O_8 . The Spectra data collected with the Maestro software were first converted to the standard AXIL format and then fitted with a model created from the qualitative information on the spectra using a Non-linear Least Square strategy of AXIL software package. Quantification of the concentration of detectable elements was made using a modified version of emission-transmission method [9].

XRD Analysis

The sample was further analyzed using X-ray diffractometry PW 1800 at the National Steel, Raw Material Exploration Agency, Kaduna Nigeria. The sample preparation consisted of pulverization and screening to obtain the required mesh size of 63 μm to 100 μm . The pulverized sample (0.5 g) was then weighed and placed in the sample holder of about 10 mm diameter and smoothened to obtain a polished sample face. The sample holder was then introduced into the sample cavity and scanned continuously at 0.020° angle interval from 2° , (2θ) to 65° (2θ) at 0.4000 second per step [10].

Optical Microscopic Analysis

Optical microscopy analysis for mineralogical investigation was carried out for the sample at the Geology Department of the University of Ilorin. The petrological slide was prepared following standard

procedure [10]. The prepared slides were observed under an optical microscope for mineralogical identification and the optical micrographs of sections of the slides were produced using Leitz R3MOT electronic device coupled with Leitz dialux 2D camera. The films were developed and printed. The interpretation of the results was done following the petrography interpretations of carbonate petrographies reported by Turker and Wright [11].

Infrared (I.R) Spectroscopic Measurement:

The I.R spectra of the sample were obtained using a Buck Scientific M500IR spectrophotometer. For the I.R measurement, about 5 mg of the solid sample was ground to very fine dispersion with a drop of nujol as mulling agent [12].

UV-Visible Spectroscopic Measurement

About 1cm^3 of the stock solution of each of the dye was measured and diluted with distilled water and their absorbance was read between 400-700nm to determine their λ_{max} using UV-VIS spectrophotometer [12]

Result and Discussion

Solubility Test

The results of the solubility and other physico-chemical tests carried out on the raw dye are shown in Tables I and II respectively. It is of interest to note that the sample was soluble in almost all the solvents with the solutions having different colours. Some of the colours appeared to be unstable as they changed after 24 h. The colour ranged from brown, red, yellow and black. The colours observed may be attributed to the existence of certain complexes involving some elements within the sample and organic species acting as ligands. The sample was found to be soluble in both polar (H_2O) and non-polar (acetone) solvents. The pH of the resulting aqueous solution shows that the sample solution was slightly alkaline. This may be due to the presence of carbonates or hydrogen carbonate of alkaline and alkaline earth metals in the samples. The dye is a complex mixture as indicated in the ash and organic contents of (51 % and 49 % respectively).

Table I: Ssolubility of the sample Yf, in different solvents with the observed colour change after 24h.

Solvent	Solubility	Colour of solution	Colour after 24hour
Deionized water	Soluble	Colourless	Golden red
Hydrogen peroxide	Soluble	Dark brown	Yellowish red
Acetone	Soluble	Light Brown	Brown
Benzaldehyde	Soluble	Wine red	Golden yellow
Acetaldehyde	Soluble	Reddish brown	Brownish Black
Ethanol	Soluble	Faint brown	Dark brown
Petroleum Ether	Insoluble	Colourless	Residue
Conc. HNO ₃	Soluble	Colourless	Golden brown
Conc. HCl	Sparingly soluble	Cloudy whitish mixture	White sediment
Methanol	Soluble	Light brown	Dark red
Diethyl ether	Soluble	Colourless	Residue
Ethylacetate	Soluble	Colourless	Red
Acetic acid	Soluble	Faint yellow	Faint yellow
Aniline	Soluble	Brown	Dark Brown

Table II: physiochemical parameters obtained for the raw dye (Yf).

Test performed	Results
Appearance of the crystal	White
pH of the aqueous solution	8.6
Max. absorption λ_{max}	464.0 nm
Ash Content	51 %
Organic content	49 %

Elemental Analysis by XRF Techniques

The results of XRF analysis of the sample YF is summarized in Table III. Twenty elements were recorded and their concentrations ranged from major to ultra-trace levels. The major elements included potassium (K) and calcium (Ca), minor elements were Ti, V, Cr, Zn, Mn and Fe trace elements were Co, Ni, Cu, As, Pb, Nb and Zr, and the ultra-trace elements included Rb, Sr, Y and Mo. The presence of Br (13.0 ppm) is in accordance with the result of optical microscopy which suggests

marine origin for the sample as the element is usually associated with the marine environment.

The results of XRF reveal that, this dye could have certain degree of toxicological effect due to the presence of some toxic elements such as As, Pb, Cr, Co and Zn in the sample. It is of interest to note that all of the first series transition elements except scandium (Sc) were recorded. The colour of the sample be linked with the formation of coloured complex compounds by some of these transition elements [13].

Table III: Elemental concentration in sample YF

Element	Conc. (ppm)	Element	Conc. (ppm)
K	4300 ppm	Zn	26.0 ppm
Ca	2600 ppm	As	21.0 ppm
Ti	700 ppm	Pb	31.0 ppm
V	345 ppm	Br	13.0 ppm
Cr	207 ppm	Rb	9.0 ppm
Mn	175 ppm	Sr	9.0 ppm
Fe	246 ppm	Y	9.0 ppm
Co	66.0 ppm	Zr	6.0 ppm
Ni	53.0 ppm	Nb	30.0 ppm
Cu	35.0 ppm	Mo	5.00ppm

XRD Analysis

The complementary results were also obtained from the XRD analysis (figure 1) which shows that the sample contains forty five different mineral phases. The identification numbers used were extracted from the American Society of Testing of Material (ASTM) files of the Joint Committee of Powder Diffraction Standard [14]. For example, Sample YF contains the following minerals with their names and identification numbers Nickeldiagua2.18-9,11($C_{18}H_{22}N_6NiO_6 \cdot H_2O$)(46-1711) Cesium fluoride iodide ($Cs_2F_2I_2$)(46-1090), Barium hydrogen phosphate ($BaH(PO_3)_3$)

(37-0285), Thallium Scandium fluoride ($TlScF_6$)(45-0902) and potassium hydrogen sulphate ($K_5H_3(SO_4)_4$) (17-0597). The presence of Thallium Scandium fluoride ($TlScF_6$) also confirmed the presence of scandium (Sc), which was not detectable in the XRF results. The other probable but very minor components with their chemical formulae and identification number were shown in Table IV and Figure 1. It is of interest to note that apart from the inorganic minerals, there were also organic components in the sample. Organic components that were found in the sample include $C_{12}H_4N_8O_{12}$, $C_6Br_4O_2$ and $C_6H_4Cl_3N$.

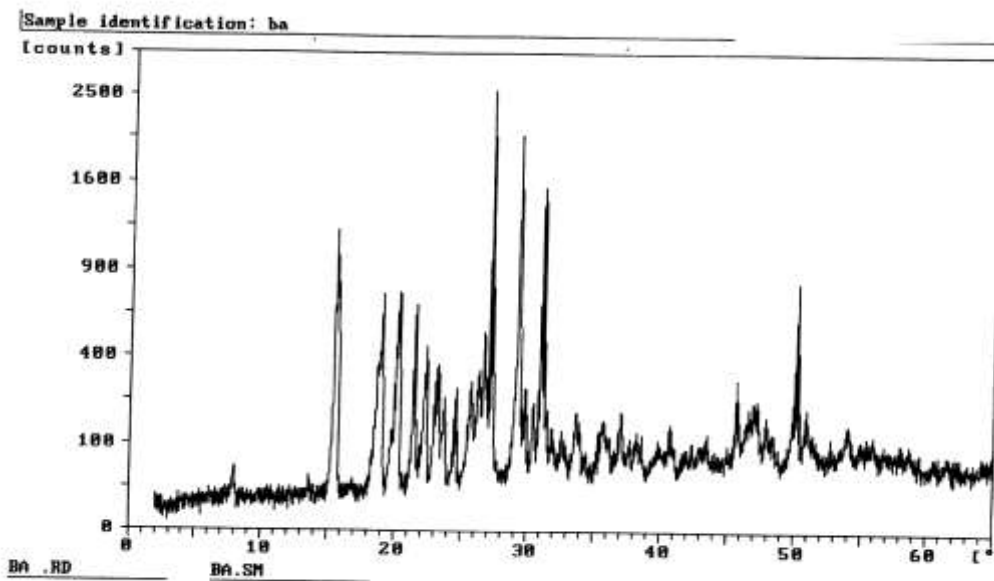


Figure 6 XRD spectrum of YF

Fig. 1: XRD spectrum of YF

Table IV: List of minerals with their chemical formula and identification numbers from ASTM files sample YF.

Card ID	Chemical formula
42-1379	$\text{Na}_{3.7}\text{Ca}_{7.4}\text{Al}_{18.5}\text{Si}_{77.5}\text{O}_{19}$
39-0225	$\text{C}_{48}\text{H}_{116}\text{N}_4\text{O}_{196}\text{Si}_{96}$
41-0569	$\text{Cs}_4\text{Al}_4\text{Si}_{20}\text{O}_{48}$
38-0293	$\text{Ca}_5\text{Cr}_2\text{SiO}_{12}$
42-0972	RbYbBr_3
42-1478	$\text{Ca}_4\text{Al}_6\text{O}_{12}\text{SO}_4$
32-0647	$\text{C}_2\text{MnO}_{4.2}\text{H}_2\text{O}$
44-0465	$\text{Nb}_{12}\text{WO}_{33}$
44-1613	$\text{C}_{12}\text{H}_4\text{N}_8\text{O}_{12}$
20-1322	$\text{Nb}_8\text{W}_9\text{O}_{47}$
42-1564	$\text{C}_6\text{Br}_4\text{O}_2$
43-0167	$\text{K}_3\text{Nb}_3\text{B}_2\text{O}_{12}$
42-1148	NaCaAlF_6
46-0600	NaCaAlF_6
44-1937	$\text{CH}_8\text{N}_3\text{O}_3\text{P}$
34-0106	$\text{Ba Cd (PO}_3)_4$
30-0197	Bi_3Y_5
38-1082	$\text{Li}_2\text{ZnGeO}_4$
36-1222	$\text{Tl}_6\text{As}_5\text{Se}_{10}$
32-1358	SnBi_2S_4
Card ID contd	Chemical formula contd
26-1493	Na_3VF_6
44-1614	$\text{C}_{12}\text{H}_4\text{N}_8\text{O}_{12}$
29-0559	$\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}$
33-1219	$\text{NaCa}_2\text{Al}_2\text{F}_4 (\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$
15-0563	SiP_2O_7

21-1183	$\text{Sr}_{10}(\text{CrO}_4)_3(\text{GeO}_4)_3\text{F}_2$
17-0383	$\text{TiSe}_{1.60}$
45-1412	$\text{Cu}(\text{Pb,Bi})_{12}\text{Bi}_4\text{S}_{18}$
46-1370	$\text{Pb}_{8.2}\text{Bi}_{4.3}\text{CuO}_{.4}\text{S}_{15}$
21-0946	PbSrCl_3
21-0946	Pb_2CrO_5
22-1477	Ti_2Te_3
17-0754	$(\text{Ca, Na})_4\text{Al}_3(\text{Al,Si})_3\text{Si}_6\text{O}_{24}$
37-1361	$\text{CdZnGe}_2\text{O}_6$
07-0379	$\text{Pb}_9\text{Sb}_3\text{S}_{21}$
20-1532	$\text{C}_6\text{H}_4\text{Cl}_3\text{N}$
27-1144	EuScO_3
45-0361	$\text{Ba}_3\text{InFeGe}_4\text{O}_{14}$
36-0533	$\text{K}_3\text{LiNb}_6\text{O}_{17}$
33-1335	SrHPO_4

Optical Microscopic Analysis

Figure 2 and Table V describe the morphology of sections of the slides prepared from the sample YF, from SEM. Sample YF (Table V) consists of mud as the groundmass. The opaque mineral observed in the sample is likely to be iron materials. Other components observed were fossil traces and algae. The rock sample also shows evidence of marine environment that has been subjected to a level of diagenesis (especially micritization and dissolution) and has not really undergone recrystallization [11]. There are evidences of rotten bioclasts (fossil material) decaying to form something like peloid (fig. 1).

It was observed that the sample apparently dissolved in Canada balsam mounting medium to give a light to dark-brown or reddish-brown colour. It contains fine-grained material dominantly (about 80 %) composed of sub-rounded to irregular shaped pigments. The pigment is dark green coloured in plane polarized light but pleochroic yellow in cross-nicol. The pigment appears dispersed with some aggregations. There were also occurrence of few (about 10%) large grains of quartz and feldspar and some (less than 10 %) light-brown to yellow finely elongated crystals of biotite.

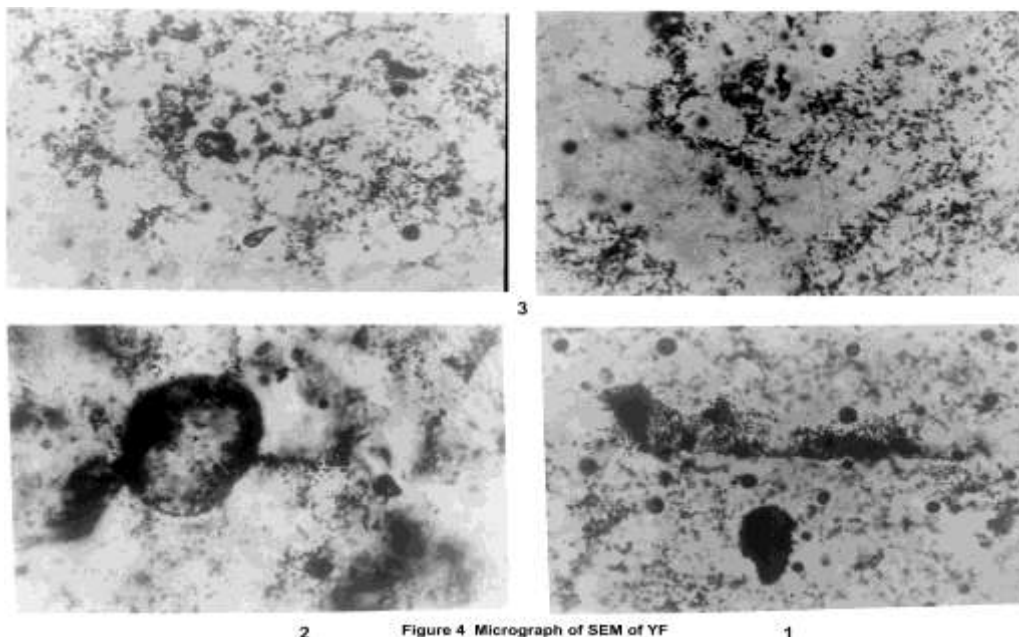


Fig 2: SEM Micrograph of YF

Table V: Observed features from optical microscopy of YF

Section	Important Petrographic Features	Remarks
1	Opaque mineral observed	Likely to be iron materials
2	Fossil and algae traces	Evidence of marine environment that has been subjected to a level of diagenesis (especially Micritization and dissolution)
3	Evidences of rotten bioclast.	Decaying materials forming something like peloid (fossil materials)

Infrared (I. R) Spectroscopic Measurement

The results of I.R analysis of the dye is presented in Table VI (figure 3). The absorptions at 1374.7, 1380.9, 1460, 2925.1 and 2931.3 cm^{-1} might probably be due to the solvent [15]. These wave numbers were marked with superscript (1) in the table. I.R band of 1617.9 cm^{-1} can be attributed to C=O stretching frequencies

of some metal chelates in the sample. Absorption peaks at 1610 and 1650 cm^{-1} have been assigned to the carbonyl C=O stretching modes, suspected for the metal chelates. Other spectra data of metal chelate complexes reported include 1525 cm^{-1} for C=C chelate ring, 1490-1520 cm^{-1} for C-O stretching, 1328-1375 cm^{-1} for C=C stretching and 1185- 1240 cm^{-1}

medium weak C-O stretching [15]. Therefore, the 1374.7 cm^{-1} from the raw complexes within the sample. The ν_{asym} C=O has been reported to be dependent on the inductive effect of the constituents, such as electron withdrawing which increase ν_{asym} C-O and electron releasing, which decrease its relative value to that of the ligands [16, 17]. Hence the little variation in the spectra observed might be due to some substituents that may be present in the sample e.g NO_2 or C_6H_5 groups. In line with one of the studies

dye sample can be assigned to C=C chelate ring of some metal chelate reported in the literature [18], I.R broad peaks in region

of $3300\text{-}3550\text{ cm}^{-1}$ could be assigned to OH stretching frequency of coordinated water in chelate spectra of Ba (II), Mn(II),Co(II), Ni(II), Zn(II) and Na. Hence I.R bands, $3192.7(\text{b})$, $3296.1(\text{b})$ and $3375(\text{w.sh})\text{ cm}^{-1}$ from the raw dye were likely due to coordinated water of some of the complex compounds in this sample.

Table VI: I R spectra data (Cm^{-1}) of the dye.

Peak	Assignment
701.8 (s)	Bending frequency in aromatic Ring
817.5 (s)	PF_2S_2 , C-C-O Sym. Stretch , Aromatic ring
937 (w)	Mo-O Stretching
1058.6 (m)	Chelate ring
1119.4 (s)	C – O Chelate ring stretch.
1253.1 (s)	Coordinated amine group
1308 (m)	Nujol
1374.7 (vs)1	nujol,C=C Chelate ring
1460 (s)1	Nujol
1514.6(w)	C-O Stretching NO_2 asym stretch, aromatic
1617.9(m)(sh)	C=O stretching
2688.1 (w), 2724.6(w)	Aromatic C-H
2925.1 (b),1	Nujol
3192.7(w) (b), 3296.1(w) (b)	O-H Stretching of coordinated water in chelate complex
3375.1(w)(sh)	-N-H

Intensities in parenthesis: b-broad, vs-very strong, s-strong, m-medium, W-Weak, Super Script 1 - Spectra due to solvent used. Sh-sharp.

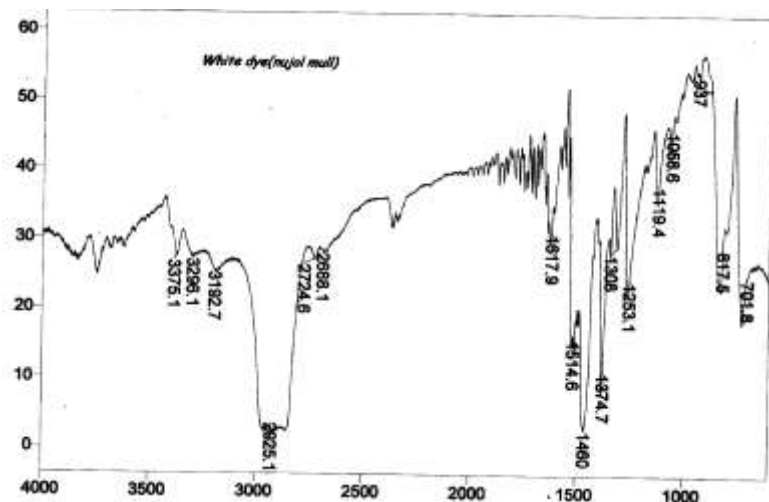


Fig. 3: IR spectrum of raw sample YF

UV-Vis Spectroscopic Measurement:

The maximum absorption band of 464.0nm for YF (fig. 4) within the visible region of electromagnetic spectrum is of interest, it shows the presence of colour imparting chromophores in the sample [19] and therefore explained its use as dye.

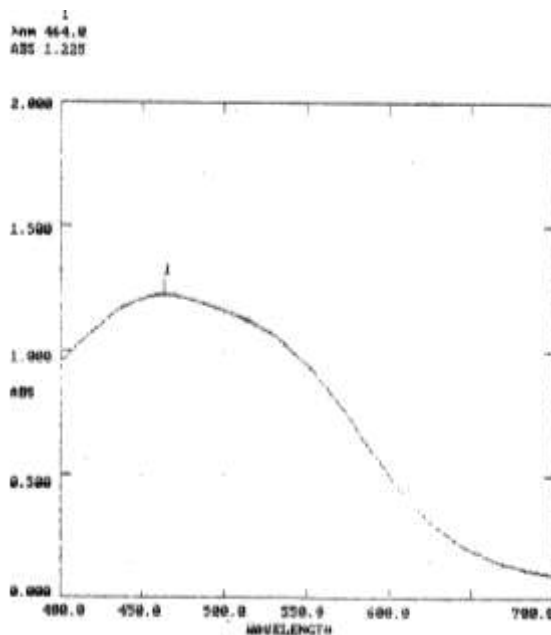


Fig. 4: The UV-VIS spectrum for sample YF showing A_{MAX} of 464.0 NM

Conclusion

It is evident from the result of the analyses of the dye that the sample is a mixture of different kinds of minerals. The minerals comprise organic and inorganic components and can be said to have been obtained from marine environment. It is also of interest to note that the mineral can serve as sources of some important elements and organic compounds which likely be aromatic in nature that can serve as raw materials for the production of other useful compounds.

Acknowledgement

The author would like to acknowledge the assistance of Drs Adekeye, O. A and Bale R. B. of Geology Department, University of Ilorin during the Microscopic analysis, and Messers Sola Oyinloye and Aremu Olagoke of National Steel Raw Materials Exploration Agency, Kaduna, Nigeria, during the XRD analysis of the samples, and Mr. Ogunleye, of Energy Research and Training Ahmadu Bello University, Zaria Nigeria during the XRF analysis.

References

1. Wayne P. A (1994). Natural dyes . J. Am. Bot. Coun. 32: 30.
2. Allen, R. L. M (1971), Colour Chemistry, ICI, Nelson pp. 6-11.
3. Chatwal, G. R. (1990) Synthetic dyes, Himalaya Publishing House, Bombay, pp 3-40.
4. Trotman, E. R. (1984) Dyeing and Chemical Technology of Textile Fibres, 6th Edn. Griffin and Comp. Ltd Britain, pp 320.
5. Barbour, J. and Simmonds, D. (1971) "Adire" Cloth in Nigeria, Institute of African Studies, University of Nigeria. Pp 43-48.
6. Picton, J. and Mack, J. (1979) African Textile, Looms, Weaving and Design; British Museum Pub. Ltd. London. Pp 36-42.
7. Adetuyi A. O., Popoola, A. V., and Lajide. L., (2003) Isolation and A Colouring Potentials of leaf extract of Teak plant (Tectone Grandis). J Chem. Soc. Nig. 28, No1, Pp 34-39.
8. Potts P. I, (1993) Energy Dispersive X-ray Spectrometry. In: A Handbook of Silicates Rock Analysis Blackie, Glasgow, Pp 286-325.
9. Potts P. J, Webb P.C. and Waston J. S. (1984) Energy Dispersive X-Ray Fluorescence Analysis of Silicate Rock, for Major and Trace Elements X-ray Spectrom Vol. 13, pp. 2-15.
10. Hutchison C. S. (1974) Laboratory Handbook of Petrography Techniques. 1st ed. Pp 1-14, A Wiley-Interscience Publication. John Wiley & Sons, New York
11. Tucker, M. E. and Wright, V. P. (1990) Carbonate Sedimentology, Oxford, (Blackwell Scientific Publications).
12. William K (1986), Organic Spectroscopy ELBS Edition, Hong Kong.
13. American Societies for Testing of Material ASTM Files (1985). Paint Pigment, Resins and Polymer 06(02) Printed in Easton, M.D, U.S.A.
14. Marry E. M. (1974) Joint Committees Of Powder Diffraction Standard U.S Geological Survey Washington D.C Philadelphia Pa
15. Junge and M. Musso; (1968): Spectrochimi Acta, 24A, 1219
16. Behnke G. T. and Nakamoto K. (1966). J. chem. Phys 45, 3113
17. Nakamoto K. (1970). Infrared spectra of inorganic and coordination compound pp 247- 256. Wiley Inter-Science, London
18. Ferraron J. R. (1971). Low Frequency Vibration In Inorganic and Coordination Compounds pp 85-95, Plenum Press, New York
19. Liprot G. F. (1984). Modern Inorganic Chemistry 4th Ed. pp 351-352 ELBS Publication, London

