

X-RAY FLOURESCENCE (XRF) ANALYSIS OF ROCK AND SOIL SAMPLES FROM A MAGNETIC INTRUSIVE ROCK IN OBA AKOKO, NIGERIA.

Faweya, E.B¹, Adesakin, G.E² and Faweya O³

Department of Physics, Faculty of Science, Ekiti State University, Ado-Ekiti, Nigeria.

febdeprof@yahoo.co.uk

Department of Physics, Faculty of Science, Ekiti State University, Ado-Ekiti, Nigeria.

adesakingbenga@gmail.com

Department of Mathematical Sciences, Faculty of Science, Ekiti State University, Ado-Ekiti, Nigeria. faweyalanre@yahoo.com

ABSTRACT

Major and minor elements concentrations were determined in rock and soils samples from and around a magnetic intrusive rock in Oba Akoko, Nigeria by X-ray fluorescence (XRF) method. The XRF analysis showed 4 major and 14 minor elements in rock and soil samples. Concentrations distribution in both media do not follow any systematic trend in all the sampling points. Calculated pollution indices such as EF and Igeo showed that the samples are uncontaminated and safe for human construction and domestic purposes. Therefore health burden is not envisaged.

Indexing terms/Keywords

XRF, Rock, Soil, Enrichment factor, Index of Geoaccumulation.

Academic Discipline And Sub-Disciplines

Physics: Radiation, Health and Environmental Physics

SUBJECT CLASSIFICATION

Physics; X-ray Fluorescence

TYPE (METHOD/APPROACH)

Quantitative and qualitative analyses of materials using XRF

INTRODUCTION

Nigerians had witnessed constant crash in the price of crude oil in the international market in the last couple of years to date. Therefore, Nigerians government is making concerted efforts to diversify Nigerian economy by shifting focus to other sources of mineral resources apart from petroleum. Aside from Ajaokuta iron and steel company, Oba Akoko a town in Ondo State Nigeria, has a magnetic intrusive rock which is likely one of the available mineral resources government is going to consider. This is as a result of its magnetic properties as seen in Fig 1.

The tremendous demands and usefulness of rocks and sand dust for various purposes such as buildings (facing stone of skyscrapers and sue of sand dusts in laying of interlocking), road construction, decking and laying of foundations and other versatile domestic used had increased in the last decade in Nigeria. Rocks have been used in a wide range of industries; ranging from building materials to domestic uses. All the industries responsible for this exploit the properties that rock can be molded into shape. This usefulness might lead to accumulation of metal and radionuclides in man's body and environment by consumption of water, plants and animals around the rock and industries using the rock.

The nature of minerals such as rock can be achieved through elemental or chemical analysis by the use of XRF technique. XRF technology has been the mostly commonly and widely accepted in nuclear analytical techniques [1, 2]. It could be described as the best available technique for the identification and quantification of all mineral present in environmental samples [3]. It usefulness in environmental analysis lies in its remarkable combination of practical and economic advantages such as; accuracy, less expensive, more accessible, no need for site specific standards, relative ease (modern instruments run under computer control with effective software), low cost of sample preparation, stability, non-destructive, fast that it allows chemical composition to be determined in seconds, elemental analysis from ¹¹Na to ⁹²U in ppm to high % concentration range, no wet chemistry (no acid, no reagents) and analysis of solids, liquids, powder, films and granules [1,4,5 6, 7,8, 9, 10, 11]. XRF can analyze multi-elements. Some of these elements are fissions yields from ²³⁵U, ²³³U and ²³⁹U [12]. It is essential to assess the extent and degree of pollution by these elements in the rock and soil samples because there is possibility these elements are adsorbed into acid rains and introduced into river and sea which will be absorbed by plants and animals which human beings depend on as food.

THEORY

X-rays are short wavelength form of electromagnetic radiation residing in the region between gamma-rays and ultraviolet radiation [7]. XRF technique depends on fundamental principle common to X-ray spectroscopy (SEM-EDS), X-ray



diffraction (XRD) and wavelength dispersive spectroscopy (Microprobe WDS) that involve the interaction between electron beam and X-rays with samples [7]. Atoms emit at specific energies when excited by X-rays. This is made possible by the behavior of atoms when they interact with radiation. The mechanism for the X-ray fluorescence of an atom takes place in the following stages. When X-ray beams illuminate the sample, it is said to be excited. The excited sample in turn emits X-rays along a spectrum of wavelength characteristic of the composition of the sample [9, 10]. The atoms in the sample absorb X-ray energy by ionizing and ejecting electrons from the lower (L-K transition i.e K_{β}) energy levels the atom becomes unstable and an outer shell (M-K transition i.e K_{β}) electron replaces the missing inner electron. This led to release of energy due to decrease in binding energy of the inner electron orbital compound with an outer one. This energy is in form of emission of characteristics X-rays indicating the type of atom present. Energy difference ΔE between initial and final electrons shells are known and fixed. Comparing the intensities of the X-rays from unknown sample to standard provides the basis for quantitative analysis of the element i.e. detecting the abundances of elements that are present in the sample [2, 7]

MATERIALS AND METHODS

SAMPLE COLLECTION

Rocks and soil samples for analyses were collected directly and around the rocks at various points using GPS machine at the base of parent rock in Oba-Akoko as summarized in Table 1. This was done to ensure samples have the same chemical composition as the parent rock. In all, 30 samples were collected for analyses. Soil samples were taken at depth 50 cm because of the distribution of trace elements [1]. Manual excavation was done and soils removed are piled on one side in order to preserve sampling purposes. All debris, vegetation and roots were removed. Samples were collected in such a way that contamination was avoided. This was achieved by the used of non-metallic tools for collection. Raw samples were packed into polythene bags, tied up and transported to the laboratory. At the laboratory samples were airdried in a clean place at room temperature for about 5 days in order to mitigate the moisture content.

SAMPLE PREPARATION

Samples were grounded manually to very fine powder with pestle and mortar to break down aggregates in order to satisfy homogeneity of XRF analysis. Samples were sieved using a siever of 60 µm size and the oversize is ground again until no grains larger than 60 µm are left. Thirty sieves made nylon were used to avoid contamination by metals [13, 14]. Pellets were pressed from the mechanical mixture of powder samples (4 g) and wax (0.9 g) using manual hydraulic press with applied load 10 tons [8]. Prepared pellets had diameter of 13 mm.

XRF SOURCES AND INSTRUMENTATION

Each pellet was irradiated for 1000 seconds at 25kV and 50 μ A. Elemental analyses were done at Centre for Energy Research and Development at Obafemi Awolowo University, Ile-Ife, Nigeria using the Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer. The spectrometer is XR-100CR model, Amptek, USA; sensitive area: 7mm², FWHM at 5.9 KeV of 55 Fe and resolution of 220 keV.

RESULTS AND DISCUSSION

X-ray fluorescence concentration of 4 major and 14 minor elements in rock and soil samples in Tables 1, 2, 3 and 4. Elements such as K, Ca, Ti and Fe which are major elements were estimated as their respective oxides in % by weight. Elements such as Cr, Mn, Ni,Cu, Zn, Ga, As, Rb, Sr, Se, Zr, Nb,V and Sc which are minor are presented in mg kg⁻¹ unit.

MAJOR ELEMENTS

The range of concentration of K_2O in major % in rock samples was 0.59-10.07% with mean value 2.63 \pm 0.1 % while it ranged from 0.64-4.63 %, with mean value 3.50 \pm 0.01% in soil samples. The concentration of CaO ranged from 0.57-5.37 % with mean value 2.17 \pm 0.1% in rock, while it ranged from 0.15-3.77 % with mean value 1.72 \pm 0.1 % in soil. However, the mean value of K and Ca in both rock and soil samples are higher than 0.24 and 0.35 % obtained in coal samples for K and Ca respectively by Kierzek [15]. TiO₂ concentrations varied from 0.14-1.04 % with mean value 0.53 \pm 0.0% in rock samples, while it varied from 0.16-1.71 % with mean value 1.14 \pm 0.0% in soil samples. Its ranges and means concentrations in both rock and soil samples was in agreement with 0.5-1.5 % by Barksdale [16]. The lowest value of Fe₂O₃ is obtained in sample 4(2.01 %) and highest value in sample 10(23.77 %) with mean value 12.64 \pm 0.1% in rock samples, while its lowest value is obtained in sample 4(1.75 %) and highest value in sample 7(14.86 %) with mean value 8.98 \pm 0.1 % in soil samples. Fe₂O₃. FeO3 ranges and means values are higher than the values obtained in columbite-tantalite (8.22 mg g⁻¹), mica (43.74 mg g⁻¹), kaolin (15.10 mg g⁻¹), flint (38.20 mg g⁻¹), feldspar (39.00 mg g⁻¹) at Ijero mining sites [17] and lot 1(52.92 mg g⁻¹), lot 2 (73.11 mg g⁻¹), lot 3 (118.76 mg g⁻¹), lot 4 (66.70 mg g⁻¹) and lot 5 (50.01 mg g⁻¹) in the dredged sediments of lower river Niger Nigeria [18]. Concentration distributions are shown in figs 2 and 3

TRACE ELEMENTS

The results revealed that Mn has the highest mean concentration (2011)ppm in rock samples followed by Sc (1021), V(620), Sr(617), Zr(515), Zn(326), Ni(139), Se(125), Ga(118), Rb(81), Nb(38), Cu(15), As(13), Cr(9.1), while the results in soil samples showed Mn (1875) ppm has the highest mean value followed by V(798), Sr(764), Zr(474), Zn(390), Sc(363), Ni(159), Rb(121), Se (120), Ga(83), Nb(46), Cu(30), As (22) and Cr(0.6). As seen in Table 3 and 4, the concentration of these trace elements vary in both rock and soil samples. The distributions do not follow any systematic trend. Elements



such as Cu, Zn, Ni and As that are hazardous have high mean concentration than background concentrations [19, 20] could pose harmful health effect and metal poisoning when the rock is used for aforementioned purposes.

ENRICHMENT FACTOR AND GEOACCUMULATION INDEX

Rock and soil pollution assessment was carried out by estimating the geoaccumulation index and enrichment factor.

Geoaccumulation index determines contamination by comparing current metal contents in the samples with average shale value. It was introduced by Muller [21] and it is given as

$$I_{geo} = log 2 \left(\frac{c_n}{KB_n}\right) [22]$$

Where C_n is the measured concentration of hazardous trace element (Cu, Ni, Zn, Mn and As), B_n is the geochemical background value in average shale of element n [23] and K=1.5 is the background matrix correction factor due to lithogenic effects. The results of Igeo obtained for both rock and soil in Table 5 varied from 0<Igeo≤2 out of scale of 7, which indicate that rock and soil samples are uncontaminated to moderately contaminated. Therefore, they can be used for various purposes without envisaging health burden.

Enrichment factor EF was estimated to assess the level of contamination and the possible anthropogenic impact of the rock and soil samples. This was estimated using the relation below [24].

$$EF = \frac{\binom{M}{Fe}_{sample}}{\binom{M}{Fe}_{background}}$$

Where EF is the enrichment factor, $\left(\frac{M}{Fe}\right)_{sample}$ is the ratio of metal and Fe concentration of the rock and soil samples

and $\left(\frac{M}{Fe}\right)_{background}$ is the ratio of metal and Fe concentration in the background. The EF calculated in Table 5 ranged

from 0.12 (rock) to 1.53(soil) which are below 1.5. These indicate that sources of these minor metals in the samples are not anthropogenic but natural.

STATISTICAL ANALYSIS

Table 6 gives statistical analysis for the major elemental concentrations of K_2O , CaO, TiO_2 and Fe_2O_3 . These analyses are arithmetic means, median, standard deviation, variance, kurtosis, maximum, minimum of their concentrations. Concentrations distributions of these major elements with their error bars and standard deviation are as shown in figs 2 and 3. The distributions indicate the spread of these elements in the samples, with Fe_2O_3 having the highest mean concentration in the rock samples indicating the magnetic property of the rock. The results of the Pearson correlation coefficient between the trace elements are presented in Table 7. Table 7 showed weak, negative and inverse correlation except few, this indicates that rock and soil samples have uncommon geochemical behaviour. i.e they are derived from different origin and not influencing each other.

CONCLUSION

XRF analyses performed on rock and soil samples showed the presence of major and minor elements. The results show that the concentrations of these elements varied widely and majority of them have higher concentration than average shale. Pollution indices (EF and Igeo) indicate that the rock and soil samples are uncontaminated and would not pose health risk to human existence.

Table 1. X-ray fluorescence concentrations of major elements in rocks samples

Samples	Locat	ions	Elements											
	Longitude(N)	Latitude(E)	K ₂ O (%)	CaO (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)								
			(Con ± SD)	(Con ± SD)	(Con ± SD)	(Con ± SD)								
1	7 ⁰ 23'48.7"	5 ⁰ 43'20.8''	1.06±0.06	2.39±0.09	0.14±0.02	5.86±0.05								
2	7 ⁰ 24'26.7"	5 ⁰ 43'20.8''	0.89 ± 0.06	0.82±0.05	0.29±0.01	10.62±0.07								
3	7 ⁰ 24'26.9"	5 ⁰ 43'24.6"	1.32±0.07	2.01±0.08	0.65±0.03	17.81±0.09								
4	7 ⁰ 25'50.0"	5 ⁰ 43'28.4"	10.07 ±0.02	0.57±0.05	0.27±0.02	2.01±0.03								
5	7 ⁰ 23'48.7"	5 ⁰ 43'20.8''	1.09±0.06	1.57±0.08	0.15±0.01	5.79±0.01								



Samples	Locat	ions		Ele	ements	
	Longitude(N)	Latitude(E)	K ₂ O (%)	CaO (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)
			(Con ± SD)	(Con ± SD)	(Con ± SD)	(Con ± SD)
6	7 ⁰ 23'48.7"	5 ⁰ 43'20.8"	0.99 ±0.06	1.78±0.08	0.39±0.02	8.02±0.06
7	7 ⁰ 24'26.9"	5 ⁰ 43'28.4"	1.20±0.06	1.53±0.07	0.98±0.04	21.84±0.09
8	7 ⁰ 23'48.7"	5 ⁰ 43'20.8"	2.99±0.11	4.55±0.13	0.78±0.03	9.55±0.07
9	7 ⁰ 23'48.7"	5 ⁰ 43'20.8"	2.83 ±0.09	5.37±0.13	1.04±0.04	16.03±0.09
10	7 ⁰ 25'50.0"	5 ⁰ 23'28.4"	0.59±0.03	0.97±0.03	0.44±0.01	23.77±0.09
11	7 ⁰ 24'26.9"	5 ⁰ 43'24.6"	1.45±0.05	2.77±0.06	0.55±0.02	20.67±0.09
12	7 ⁰ 25'50.0"	5 ⁰ 43'28.4"	4.13±0.13	1.81±0.08	0.59±0.03	14.79±0.08
13	7 ⁰ 23'48.7"	5 ⁰ 43'20.8"	4.64±0.13	1.96±0.09	0.88±0.03	17.96±0.09
14	7 ⁰ 25'50.0"	5 ⁰ 43'28.4"	1.55±0.08	2.40±0.09	0.39±0.02	11.63±0.07
15	7 ⁰ 23'48.7"	5 ⁰ 43'20.8"	4.65±0.14	2.13±0.09	0.45±0.03	3.31±0.04
Range			059-10.07	0.57-5.37	0.14-1.04	2.01-23.77
Mean			2.63±0.07	2.17±0.08	0.53±0.02	12.64±0.07

Table 2 :X-ray fluorescence concentrations of major elements in soil samples

Samples 1 2 3 4 5 6 7	Locat	ions	Elements										
	Longitude(N)	Latitude(E)	K ₂ O (%)	CaO (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)							
			(Con ± SD)	(Con ± SD)	(Con ± SD)	(Con ± SD)							
1	7 ⁰ 23'48.7"	5 ⁰ 43'20.8''	4.57±0.13	1.76±0.08	1.40±0.04	13.04±0.08							
2	7 ⁰ 24'26.7"	5 ⁰ 43'20.8''	2.90±0.11	1.14±0.07	0.64±0.03	4.99±0.05							
3	7 ⁰ 24'26.9"	5 ⁰ 43'24.6"	3.35 ± 0.11	2.23±0.09	1.31±0.04	11.42±0.07							
4	7 ⁰ 25'50.0"	5 ⁰ 43'28.4"	2.95±0.11 ±	1.97±0.08	1.17±0.04	8.70±0.06							
5	7 ⁰ 23'48.7"	5 ⁰ 43'20.8"	4.06±0.12	1.76±0.08	1.43±0.05	10.66±0.07							
6	7 ⁰ 23'48.7"	5 ⁰ 43'20.8''	0.64 ±0.03	0.15±0.01	0.16±0.09	1.75±0.02							
7	7 ⁰ 24'26.9"	5 ⁰ 43'28.4"	4.63±0.13	2.01±0.08	1.71±0.05	14.86±0.08							
8	7 ⁰ 23'48.7"	5 ⁰ 43'20.8"	2.98 ± 0.11	1.32±0.07	0.86±0.04	6.51±0.05							
9	7 ⁰ 23'48.7"	5 ⁰ 43'20.8''	3.50±0.12	2.50±0.09	1.08±0.04	10.96±0.07							
10	7 ⁰ 25'50.0"	5 ⁰ 23'28.4"	4.53±0.09	1.61±0.06	1.24±0.03	8.88±0.04							
11	7 ⁰ 24'26.9"	5 ⁰ 43'24.6''	4.55±0.12	1.65±0.05	1.31±0.03	8.57±0.07							
12	7 ⁰ 25'50.0"	5 ⁰ 43'28.4''	1.95±0.06	0.88±0.04	0.52±0.02	3.56±0.03							
13	7 ⁰ 23'48.7"	5 ⁰ 43'20.8''	4.45±0.13	1.27±0.06	1.70±0.05	13.08±0.08							
14	7º25'50.0" 5º43'28		3.27±0.11	1.86±0.08	1.17±0.04	7.15±0.06							
15	7 ⁰ 23'48.7"	5 ⁰ 43'20.8''	4.22±0.09	3.77±0.08	1.42±0.03	10.64±0.05							



Samples	Locat	ions		Ele	Elements						
	Longitude(N)	Latitude(E)	K ₂ O (%)	CaO (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)					
			(Con ± SD)	(Con ± SD)	(Con ± SD)	(Con ± SD)					
Range			0.64-4.63	0.15-3.77	0.16-1.71	1.75-14.86					
Mean			3.50±0.01	1.72±0.01	1.14±0.05	8.98±0.06					

Table 3: X-ray fluorescence concentrations of minor or trace elements in rock samples

Sample	Elements (ppm) Cr Mn Ni Cu Zn Ga As Rb Sr Se Zr Nb V Sc														
	Cr	Mn	Ni	Cu	Zn	Ga	As	Rb	Sr	Se	Zr	Nb	V	Sc	
	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con	
	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	
1	6±1	1154± 62	162± 14	19±2	197±1 9	164± 18	12±3	71±1 0	763±1 00	151± 15	274±4 6	59±1 1	441±6 4	1837± 202	
2	ND	1164± 61	193± 15	13±2	237±2 2	25±7	11±3	65±1 0	237±4 9	171± 17	174±3 8	31±8	526±7 0	266±7 6	
3	ND	2424± 88	98±1 1	14±2	328±2 5	49±1 0	ND	38±8	611±8 8	140± 15	745±7 8	32±8	872±9 0	1085± 100	
4	ND	562±4 5	291± 17	21±2	185±1 7	148± 12	54±5	135± 10	929±1 10	74±7	173±3 3	26±5	692±6 8	173±3 3	
5	ND	1280± 65	210± 16	19±2	417±2 8	163± 18	10±2	69±1 0	519±7 8	226± 18	175±3 7	39±9	552±7 1	1099± 100	
6	ND	1325± 66	72±9	13±2	273±2 3	57±1 1	15±3	46±8	411±6 7	76±1 1	395±5 6	35±8	427±6 3	1392± 175	
7	ND	3482± 105	77±1 0	ND	271±2 3	ND	10±2	53±9	306±5 7	110± 14	219±4 3	22±7	1178± 100	492±1 00	
8	ND	2829± 98	175± 14	27±3	328±2 4	164± 17	10±2	107± 11	746±9 8	95±1 1	675±7 1	36±8	884±9 0	2455± 230	
9	ND	2810± 97	176± 14	ND	371±2 6	241± 22	ND	137± 14	1025± 125	160± 15	955±8 6	47±1 0	958±9 4	2210± 221	
10	ND	2482± 67	133± 13	ND	365±2 7	181± 21	9±2	63±1 0	337±6 1	86±1 2	191±4 0	40±1 0	357±3 5	533±6 5	
11	ND	3019± 87	115± 12	34±3	530±3 2	121± 16	12±3	162± 16	982±1 23	135± 15	898±8 6	60±1 1	410±4 5	866±9 8	
12	ND	2259± 86	75±9	ND	280±2 3	80±1 2	12±3	60±9	440±7 0	79±1 1	572±6 7	33±8	886±8 8	354±8 4	
13	11±1	2404± 88	96±1 1	20±2	593±3 4	175± 18	17±3	70±1 0	742±1 00	105± 12	253±4 5	40±9	774±8 2	284±7 5	
14	ND	1919± 79	90±1 0	29±3	380±2 7	147± 17	21±3	88±1 1	590±8 5	158± 16	1737± 118	40±9	748±8 4	2182± 219	
15	ND	1049± 61	126± 11	16±2	138±1 5	58±9	8±2	52±7	620±8 4	104± 10	293±4 5	28±6	655±7 2	81±40	
Range	ND- 11	562- 3482	72- 291	13- 34	138- 593	25- 241	8-54	38- 162	237- 1025	74- 171	173- 1737	22- 60	357- 1178	81- 2455	
Mean	1.1±0. 13	2011± 77	139± 12	15±2	326±2 4	118± 14	13±2	81±1 0	617±8 6	125± 13	515±5 9	38±8	620±7 4	1021± 121	

June 2016



Table 4:X-ray fluorescence concentrations of minor or trace elements in soil samples

Sample				E	lements	(ppm)								
	Cr	Mn	Ni	Cu	Zn	Ga	As	Rb	Sr	Se	Zr	Nb	V	Sc
	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con	Con
	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd	±sd
1	ND	2243± 86	137± 13	28±3	294±2 3	146± 16	ND	162± 14	1476± 166	84±1 1	521±6 3	62±1 1	1065± 96	176±5 9
2	ND	877±5 5	151± 13	32±3	533±3 1	218± 19	24±4	73±9	684±9 2	129± 13	227±4 1	44±8	562±6 8	ND
3	ND	2304± 88	180± 14	89±3	491±3 0	84±1 2	42±5	154± 14	829±1 07	114± 13	507±6 3	79±1 2	630±7 5	441±9 5
4	ND	2231± 87	132± 12	28±3	272±2 2	1041 4±	15±3	127± 13	741±9 8	178± 16	482±6 1	33±8	854±8 7	386±8 9
5	9±1	1766± 77	192± 15	39±3	458±2 9	103± 14	20±3	167± 14	1340± 153	245± 18	706±7 3	60±1 0	891±8 8	880±1 32
6	ND±	361±2 0	329± 11	ND	345±1 5	71±6	77±4	24±3	218±3 0	122± 7	233±2 5	39±5	118±1 8	ND
7	ND	2868± 98	132± 12	22±2	390±2 7	ND	26±4	192± 16	930±1 17	106± 12	635±7 0	64±1 1	1166± 100	211±6 5
8	ND	1801± 78	118± 12	12±2	530±3 1	75±1 1	11±2	96±1 1	511±7 6	48±8	306±4 8	46±9	598±7 1	157±5 5
9	ND	2369± 89	125± 12	44±3	471±2 9	ND	14±3	136± 13	904±1 14	142± 14	663±7 1	52±1 0	917±9 0	512±1 00
10	ND	2003± 58	157± 9	13±1	274±1 6	47±6	23±2	149± 9	485±6 0	55±6	515±4 4	33±5	1141± 69	ND
11	ND	2350± 67	1104 5±	113± 10	531±1 6	43±7	21±3	187± 11	495±6 1	145± 15	514±4 2	43±8	565±6 2	ND
12	ND	875±3 9	68±6	15±1	121±1 0	36±5	15±2	52±5	342±4 6	45±5	387±3 8	15±3	380±4 0	180±4 2
13	ND	1713± 75	129± 12	ND	439±2 9	125± 15	20±3	138± 13	1021± 125	194± 16	779±7 8	36±8	1143± 99	ND
14	ND	1916± 81	156± 13	21±2	355±2 5	82±1 2	7±2	60±8	759±1 00	72±1 0	383±5 3	51±9	824±8 4	473±9 7
15	ND	2441± 65	269± 12	ND	350±1 8	114± 10	14±2	101± 8	731±8 2	116± 9	258±3 1	34±5	1122± 70	2031± 145
Range	ND-9	361- 2868	68- 329	12- 113	121- 533	36- 218	7-77	24- 192	218- 1476	45- 245	227- 779	15- 79	118- 1166	157- 2031
Mean	0.6±0.	1875± 71	159± 14	30±2	390±2 3	83±1 0	22±3	121± 11	764±9 5	120± 12	474±5 3	46±8	798±7 4	363±5 9



Table 5:Average concentration of selected hazardous trace element, average shale (ppm), EF and Igeo values in rock and soil samples.

Elements	Average shale	Mean \	/alues	Enrichme (El		Geoaccui Index (Ige	
		Rock	Soil	Rock	Soil	Rock	Soil
Cu	45	15	30	0.12	0.25	1.11	2.22
Zn	95	326	390	1.28	1.53	1.14	1.37
Ni	68	139	159	0.76	0.87	0.68	0.78
Mn	850	2011	1875	0.90	0.82	0.79	0.74
As	13	13	22	0.37	0.63	0.33	0.56

Table 6:Descriptive statistics of major elemental concentration

Parameters			E	lemental cor	ncentration	Elemental concentrations														
			Rock			So	oil	Fe ₂ O ₃ 8.98 8.88 3.69 13.61 -0.38 -0.41 14.86 1.75												
	K₂O	CaO	TiO ₂	Fe ₂ O ₃	K₂O	CaO	TiO ₂	Fe ₂ O ₃												
Mean	2.63	2.17	0.53	12.64	3.50	1.75	1.14	8.98												
Median	1.45	1.96	0.45	11.63	3.50	1.76	1.24	8.88												
Standard deviation	2.49	1.29	0.29	6.93	1.13	0.81	0.43	3.69												
Sample variance	6.21	1.67	0.08	48.08	1.28	0.65	0.19	13.61												
Kurtosis	5.23	2.12	-0.81	-1.22	1.58	2.64	0.54	-0.38												
Skewness	2.12	1.43	0.43	0.05	-1.23	0.67	-0.92	-0.41												
Maximum	10.07	5.37	1.04	23.77	4.63	3.77	1.71	14.86												
Minimum	0.59	0.57	0.14	2.01	0.64	0.15	0.16	1.75												
Range	9.48	4.80	0.90	21.76	3.99	3.62	1.55	13.11												

4049 | Page

council for Innovative Research www.cirworld.com



TABLE 7 Pearson correlation coefficients of minor element in both rock and soil samples.

Variables	Mn	Mn(s)	Cr	Cr(s)	Ni	Ni(s)	Cu	Cu (s)	Zn	Zn (s)	Ga	Ga(s)	AS	As(s)	Rb	Rb(s)	Sr	Sr(s)	Se	Se(s)	Zr	Zr(s)	Nb	Nb(s)	٧	V(s)	Sc	Sc(s)
Mn	1			.,,																								
Mn(s)	0.33	1																										
Cr	-0.02	0.01	1																									
Cr(s)	-0.23	-0.04	-0.1	1																								
Ni	-0.51	0.15	-0.1	0.32	1																							
Ni(s)	-0.45	-0.27	-0.2	0.14	-0.16	1																						
Cu	-0.21	0.07	0.16	0.1	0.19	0	1																					
Cu (s)	0.3	0.35	-0.2	0.07	0.06	-0.3	0.3	1																				
Zn	0.54	0.03	0.4	0.2	-0.26	-0.3	0.3	0.3243	1																		Ш	
Zn (s)	0.29	0.18	-0	0.16	0.14	0	0.4	0.4698	0.41	1																		
Ga	0.05	0.19	0.3	0.18	0.39	-0.3	0.2	-0.025	0.42	0.01	1																	
Ga(s)	-0.7	-0.32	0.34	0.1	0.37	0.2	0.4	-0.151	-0.2	0.18	-0.2	1																
AS	-0.5	-0.04	0.06	-0.1	0.51	-0.1	0.3	-0.195	-0.2	-0.4	0.1	0.2	1															
As(s)	-0.02	-0.49	-0.2	-0	-0.36	0.7	-0.2	0.0085	0.01	0.09	-0.5	-0.1	-0.1	1														
Rb	0.16	0.3	-0.1	-0.1	0.47	-0.5	0.4	0.4378	0.3	0.27	0.55	-0.2	0.34	-0.4	1													
Rb(s)	0.37	0.79	0.19	0.25	0.18	-0.3	0	0.5155	0.3	0.3	0.19	-0.2	-0.1	-0.3	0.25	1												
Sr	0.06	0.44	0.21	-0.1	0.36	-0.3	0.5	0.3908	0.26	0.21	0.63	-0.2	0.23	-0.4	0.79	0.3	1											
Sr(s)	-0.18	0.48	0.47	0.46	0.32	-0.1	0.1	0.0722	0.04	0.16	0.28	0.29	-0.1	-0.5	-0.1	0.6	0.204	1										
Se	-0.1	0.14	-0	0.65	0.23	-0	0.2	0.3956	0.23	0.5	0.17	0.28	-0.3	-0.3	0.06	0.3	0.032	0.65	1									
Se(s)	-0.3	0.08	0.24	0.61	0.42	0.2	0.2	0.1994	0.33	0.36	0.15	0.23	0.24	0.12	0.19	0.4	0.266	0.46	0.45	1								
Zr	0.32	0.1	-0.2	-0.2	-0.31		0.3	0.309		0.15		-0.3		-0.2	0.35	-0	0.326	-0.2	0.19	-0.3	1							
Zr(s)	0.37	0.49	0.47	0.37	0.06	-0.4	-0.1	0.2193	0.59	0.11		-0.3	-0.1	-0.2	0.18	0.7	0.322	0.62	0.31	0.52	-0.1	1						
Nb	0.14	0.1	0.32	0.03	-0.02		0.4	0.4313		0.17		-0	-0.2	-0.3	0.47	0.3	0.519	0.25	0.34	0.01	0.3	0.26	1					
Nb(s)	0.19	0.46	-0	0.24	-0	0.1	0.1	0.4588		0.53	-0.1	0.01	-0.4	0.06	-0.1	0.5	0.043		0.59	0.18	0.15	0.32		1				
V	-0.03	-0.13	0.06	-0.1	0.14	-0.2	0.1	0.0028	0.11	0.05	0.39	0.02	-0	-0.2	0.19	-0	0.445	-0.1	0.01	-0	0.42	-0.04	-0	-0.14	1			
V(s)	0.09	0.73	0.39	0.08	0.17	-0.2	-0.1	-0.189	0.05	-0	0.31	-0	0	-0.6	-0	0.6	0.113	0.64	0.15	0.16	-0.2	0.57	0.01	0.198	0	1		
Sc	0.22	0.04	-0.1	0.03	-0.01	-0	0.3	0.0882	0.12	0.28	0.48	-0.2	-0.3	-0.1	0.27	-0	0.341	0.13	0.3	-0.3	0.62	-0.02	0.46	0.417	0	-0.2	1	
Sc(s)	-0.35	0.34	-0.2	0.27	0.12	0.4	0	-0.147	-0.4	-0	-0.1	0.07	-0.1	-0.2	-0.2	0	0.099	0.23	0.18	0.19	-0	-0.13	-0.3	0.031	0	0.3	-0	1

Mn=rock samples., Mn(s)=soil samples





Fig 1. Rock samples from parent rock attracted by a magnet.

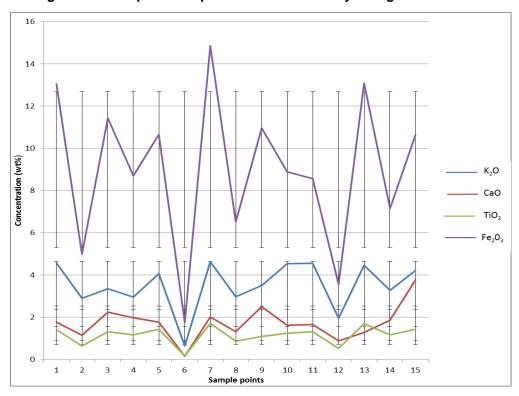


Fig 2: Concentration distribution in soil samples



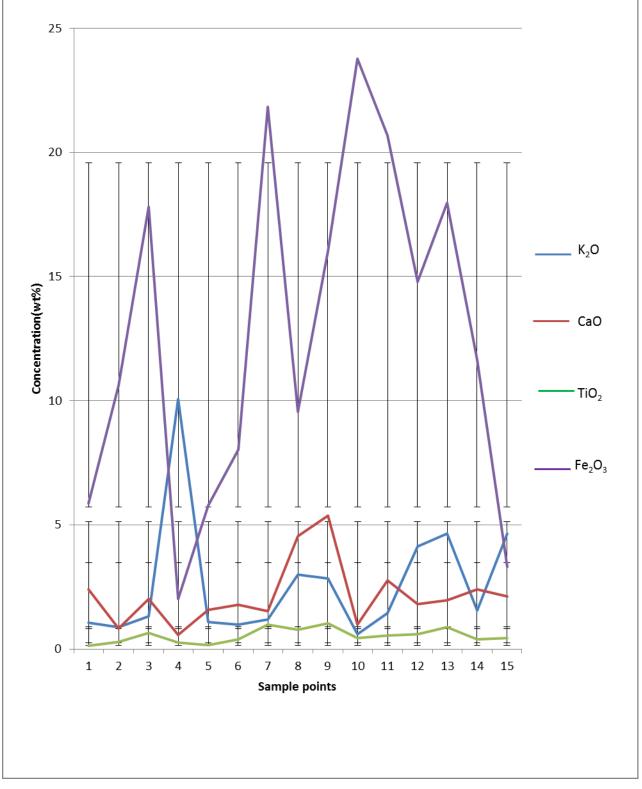


Fig 3. Concentration distribution in rocks samples

June 2016



REFERENCES

[1]IAEA 1997. Sampling, storage and sample preparation procedure for X-ray fluorescence analysis of environmental materials, 7-65

[2]Kalnicky, D.J and Singhwi, R 2001. Field portable XRF analysis of environmental samples. Journal of Hazardous Materials 83: 93-122.

[3]Jan, S, Victor. A.D, Douglas, K.M, Jean C.C.H and Dennis, D.E 2001. Quantitative X-ray diffraction analysis of claybearing rocks from random preparations. Clays and Clay Minerals, 49, 6 (Galley 59).

[4]IAEA 2003. International Atomic Energy Agency. Collection and preparation of bottom sediment samples for analysis of radionuclides and trace elements IAEA-TECDOC-1360. IAEA, Vienna, Austria, 2003b.

[5]Shackley, M.S 2005. Obsidian: Geology and Archaelogy in the North American Southwest. University of Arizona press, Tucson.

[6] Yukiko, I, Atsushi, B, Shintaro, K, Shin-Ichiro, W and Kouichi, T 2010. Experimental parameters for XRF analysis of soils. International Centre for Diffraction Data (ICDA) 248-255.

[7]Shackley, M.S 2011. X-ray fluorescence spectrometry (XRF) in Geoarchaeology. Springer Science+ Bussiness Media LLC (2011) DOI 10.1007/978-1-4419-6886-9-2: 7-44.

[8]Neuwirthova, L, Matejka, V, Mamulova, K.K and Tomasek, V 2012. X-ray fluorescence spectrometry analysis of clay/ZnO composites. NANOCON. Brno, Czech Republic, Eu.

[9]Andrianainarivelo, M and Ranaivoson, J 2013. Physico-chemical analysis for differents types of clay soils in the areas of Analamanga Itasy and Vakinankaratra. International Journal of Materials and Chemistry 3(5): 99-105.

[10]Karl, W and Andy, B 2016. X-ray fluorescence Geochemical Instrumentation and Analysis. Retrieved 2016.

[11]Oxford Instruments 2016. XRF explained. Retreived 2016.

[12]Edward, M.B, Harold, D.K and Thomas, R.M 2002. Nuclides and Isotopes: Chart of the Nuclides 16th (Ed): 47-51.

[13] Jenkins, R, Gould, R.W, Gedcke, I 1981. Quantitative X-ray Spectrometry, Marcel Dekker, New York Basel (cross ref)

[14]Injuk, J and Van G.R 1993. Sample preparation for XRF. In Handbook of X-ray Spectrometry: Methods and Tecniques (Van Grieken, R.E and Markowicz, A.A, Eds) Marcel Dekker, Inc. New York NY 657-692 (cross ref)

[15]Kierzek J, Malozewska-Bucko, B, Bukowski, P, Parus, J.L, Ciurapinski, A, Zaras, S, Kunach, B and Wiland, K 1999. Assessment of coal and ash environment impact with the use of gamma- and x-ray spectrometry. J. radioanal. Nucl Chem 240(1):39-45. 10.1007/BF02349134

[16]Barksdale, J 1968. Titanium: In the Encyclopedia of the chemical elements. Edited by: Hampel CA, Reinhold Book Corporation, New Yor: 732-738 LCCN 68-29938.

[17]Faweya, E.B and Oniya E.O 2012. Radiological safety assessment and physico-chemical characterization of soil mixed with mine tailings used as building materials from Oke-kusa mining sites in Ijero, Nigeria. Nature and Science 10(5): 69-71.

[18] Faweya, E.B, Oniya, E.O and Ojo F.O 2013. Assessment of radiological parameters and heavy metal contents of sediment samples from lower Niger River, Nigeria. Arabian Journal for Science and Engineering 38(7): 1903-1908.

[19] Taylor,S and McLennan, S. 1995. The geochemical evolution of the continental crust. Reviews of Geophysics 33:241-265.

[20]Wedepohl, H 1995. The composition of the continental crust. Geochimica et Cosmochimica Acta 59:1217-1239.

[21] Muller, G 1969. Index of geoaccumulation in sediments of the Rhine River. Geol J, 2:109-118.

[22]Matini, I, Ongoka, P.R and Tathy, J.P 2011. Heavy metals in soil on spoil heap of an abandoned lead ore treatment plant SE Congo-Brazzaville. African J.Environ Sci.Tech 5:89-97

[23]Turekian, K.K and Wedepohl, K.H 1961. Distribution of the elements in some major and units of the earth's crust. Geol.Soc.Am 72:175-192.

[24] Habes, G and Nigem Y 2006. Assessing Mn, Fe, Cu, Zn and Cd pollution in bottom sediments Wad, Al-Arab Dam, Jordan Chemosphere www.elsevier.com/locate/chemosphere.