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Assessment of Major Minor and Trace Elements in Soils and Sediments around a Refinery

**Complex using Instrumental Neutron Activation Analysis** 

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# ABSTRACT

In this study, Instrumental Neutron Activation Analysis (INAA) was used to investigate the major, minor, and trace elements in soil around the Kaduna Refining and Petrochemical Company in Nigeria. Various degrees of pollution are associated with the upstream and downstream sectors of the oil industry with attendant negative health and environmental consequences. We can only deal with these problems by quantifying the pollutants in air, water, soil and sediments, and notify the appropriate authority so as to take necessary measures towards remediation. Samples were collected from fifteen different locations around the refinery complex and irradiated at thermal neutron dose rates of 5 x 10<sup>11</sup> and 2.5 x 10<sup>11</sup> ncm<sup>-2</sup>s<sup>-1</sup> (inner and outer irradiation channels respectively) in a miniature neutron source reactor (code-named NIRR-1) at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria Nigeria. Twenty – five elements (Mg, Al, Ti, V, Mn, Na, K, As, La, Sc, Cr, Fe, Co, Zn, Rb, Sb, Cs, Ba, Eu, Yb, Lu, Hf, Ta, Th, and Dy) were detected. Wide range of variations in elemental concentrations was observed in the soils and sediments. Elemental concentrations varied from 1.72 µg/g (Ta) to 5.6 % (Fe) in the soils and 1.50 µg/g (Ta) to 6.6 % (Fe) in the sediments. Though some elements including Al, Ti, V, K, occurred at background levels, others including as Fe, Zn, As, Lu, were in substantial amounts with background loading factors of between 1.05 and 9.87, while results also generally revealed enrichment in elemental concentrations in sediments as compared to those of the soils.

**Keywords**: Major minor and trace elements, soils and sediments, Kaduna Nigeria, INAA, NIRR-1

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# **INTRODUCTION**

Petroleum refining involves different processes including distillation, thermal cracking, catalytic, and treatment processes. Various treatment methods are used to remove non-hydrocarbons, impurities, and other constituents that could adversely affect the properties of finished products or reduce the efficiency of the conversion processes. Consequently, hazardous and non-hazardous wastes of different forms are generated. Many refineries intentionally or unintentionally release liquid hydrocarbons and other forms of wastes into ground water and surface water. This practice often results in pollution which affects both aquatic and terrestrial ecosystems with destruction of forests and farm lands [1, 2].

Pollutants associated with petroleum refining include volatile organic compounds (VOCs), CO, SO<sub>x</sub>, NO<sub>x</sub>, particulates, NH<sub>3</sub>, H<sub>2</sub>S, metals, spent acids, and other numerous toxic organic compounds (this study dwelt only on elemental analysis of soils and sediments). These are usually discharged as air emissions, waste water, or solid waste, which in most cases are untreated. Air emissions constitute the largest source of untreated wastes released into the environment [3]. Unfortunately also, a large amount of the air emissions are again returned to the soil and water as their final sink as a result of rainfall and inertial impaction. The presence of pollutants in the environment can adversely affect the potability of water and also lead to occurrence of soil chemistry changes, with negative bearing on the health of human and animal lives, and by extension, the socio-economic index of a nation.

Various degrees of pollution are associated with the upstream and the downstream sectors of the oil industry with attendant health effects and environmental consequences. As long as the oil exploration, production, and refining processes continue, we shall continue to contend with the environmental problems posed by these activities while we also find a way of reducing or eliminating the pollutants. This, we can be achieved by quantifying the pollutants in air, water, soil, and sediments, and notify the appropriate authority so as to take necessary measures towards remediation. The technique of instrumental neutron activation analysis was employed using the Nigeria Research Reactor -1(NIRR - 1) at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria Nigeria to quantify the metal pollutants.

Neutron activation analysis is a veritable analytical tool that has been used over the years for elemental analysis, cross-sections and other nuclear data determinations [4-6]. Figure 1 presents the schematic of the neutron activation process. In the technique, a stable isotope is made

radioactive by bombarding the isotope called the target nucleus with a neutron. The radioactive nucleus emits prompt gamma rays immediately following activation (PGNAA), and after a period of decay, delayed gamma (decay gamma) corresponding to different energy peaks which are characteristic of specific elemental compositions are emitted (DGNAA). These are then measured using the gamma ray spectrometric analysis. Each element emits gamma radiation of discrete energy values. Energy peaks in the gamma spectrum are then used to identify which elements are present in a sample.



Figure 1. Illustration of the Activation process [7]

The procedure commonly used to determine the concentration (in ppm or  $\mu g/g$ ) of elements in the unknown sample relative to the standard can be determined using the expression

$$\frac{A_x}{A_s} = \frac{m_x}{m_s} \cdot \frac{\left(e^{-\lambda T_d}\right)_x}{\left(e^{-\lambda T_d}\right)_s} \tag{1}$$

where  $m_x =$  mass of the element in the sample,  $m_s =$  mass of the element in the standard,  $T_d =$  decay time, and  $\lambda =$  decay constant for the isotope

NIRR-1 is a miniature Neutron Source Reactor (MNSR) and has a tank-in-pool structural configuration with a nominal rating of 31kW and a neutron flux of  $10^{12}$  n/cm<sup>2</sup>/s. The reactor is fuelled by highly enriched uranium. Light water serves a dual purpose of the moderator and by the natural convection process as the coolant. The fuel assembly has beryllium as the reflector. It is specifically designed for neutron activation analysis (NAA), hence, it is capable of being used for analysis of trace, minor, and major elements in different sample matrices.

The neutron flux parameters of miniature neutron source reactors are known to be very stable, thus lending it to the use of semi-absolute NAA method [8, 9]. NIRR-1 was critical in 2004 and has been used for the analysis of geological and biological samples [6].

The aim of this study is to assess the level of pollution in soils and sediments around the Kaduna Refinery. The objectives include:

- i) To carry out quality control and quality assurance of the facility used
- ii) Determination of the major, minor, and trace elements in the soils and sediments
- iii) Quantification of the above elements in the soils and sediments of the study area
- iv) To evaluate the background loading factor (BLF)

### MATERIALS AND METHODS

#### The Study Area

The Kaduna Refining and Petrochemical Company (KRPC) lies in the southern area of Kaduna city, occupying an area between latitude  $10^{\circ}24'22.32'' - 10^{\circ}25'18.8''$  N and longitude  $7^{\circ}29'9.6'' - 7^{\circ}29'55.2''$  E.

#### **Sample Collection and Preparation**

Surface soil samples were collected from farms along the effluents discharge track and other farms surrounding the refinery complex. These samples which were collected using a core sampler were stored in polyethylene bags which were thoroughly washed prior to sampling. While sampling, attention was given to farm lands where the river water-mixed-with the effluents was used for irrigation. Soil samples were also collected from the sludge pit where oil wastes were dumped. Samples of sediments were also collected along the discharge track and from two rivers (Rido river and Romi river) into pre-washed plastic bottles with lids using a plastic sampling tube which was thoroughly washed after each sampling. Both the soil and sediment samples were then taken to the laboratory at the Centre for Energy Research and Training, Ahmadu Bello University Zaria, and dried at 100°C for 48 Hours to ensure complete dryness.

A four digit weighing balance (Metler AE 166, Delta range) was used to measure 0.50 g of each sample into pre-cleaned polyethylene bags and sealed with a hot soldering iron into 7cm<sup>3</sup> rabbit capsules according to [6]. Thereafter, the sample capsules were packaged into bigger vials in readiness for irradiation.

### **Sample Irradiation and Counting**

The vials containing the rabbit capsules were sent to the reactor irradiation sites using the pneumatic transfer system called the rabbit system. NIRR-1 has four irradiation channels (sites): B1, B2, B3, and B4. B1 and B3 are called the inner irradiation channels; while B2 and B4 are the outer irradiation channels with  $B_1$  being dedicated solely to those nuclides with very short half-lives.Sample irradiations were done based on two protocols – short irradiation for short-lived elements and long irradiation for long-lived elements and these were followed by the process referred to as counting (Table 1).

Neutron flux /irradiation channel	Procedur e	T <sub>irr</sub>	$T_d$	$T_m$	Activation products
$1x10^{11}$ n/cm <sup>2</sup> s /outer irradiation channels (B4, A2)	S1	2 min	2-15 min	10min	<sup>28</sup> Al, <sup>27</sup> Mg, <sup>38</sup> Cl, <sup>49</sup> Ca, <sup>66</sup> Cu, <sup>51</sup> Ti, <sup>52</sup> V, <sup>116m</sup> In
	S2	2 min	3-4h	10min	<sup>24</sup> Na, <sup>42</sup> K, <sup>165</sup> Dy, <sup>56</sup> Mn, <sup>152m</sup> Eu
5×10 <sup>11</sup> n/cm <sup>2</sup> s /inner irradiation	L1	6h	4-5d	30min	<sup>24</sup> Na, <sup>42</sup> K, <sup>76</sup> As, <sup>82</sup> Br, <sup>140</sup> La, <sup>153</sup> Sm, <sup>198</sup> Au,
Channels (B1, B2, B3, and A1)	L2	6h	10-15d	60min	<ul> <li><sup>139</sup>Np(U), <sup>72</sup>Ga, <sup>122</sup>Sb, <sup>46</sup>Sc,</li> <li><sup>141</sup>Ce, <sup>60</sup>Co, <sup>51</sup>Cr, <sup>134</sup>Cs, <sup>152</sup>Eu,</li> <li><sup>177</sup>Lu, <sup>131</sup>Ba, <sup>86</sup>Rb, <sup>182</sup>Ta,</li> <li><sup>160</sup>Tb, <sup>175</sup>Yb, <sup>233</sup>Pa(Th), <sup>65</sup>Zn,</li> <li><sup>59</sup>Fe, <sup>181</sup>Hf.</li> </ul>

Table 1. Typical irradiation and counting schemes [6]

The NIRR-1 uses two hyper-pure germanium (HpGe) detectors that operate at liquid nitrogen temperature. The computer-coupled multichannel analyzer sorts the delayed gamma according to their energies. The gamma ray acquisition system used the computer software (MAESTRO - 32) for the measurement of associated radioactivity. Finally, the background loading factor (BLF) was evaluated using:

$$BLF = \frac{C_{sample}}{C_{background}} \tag{2}$$

where C<sub>sample</sub> and C<sub>background</sub> are the concentrations of each element in the sample and the background respectively.

# **RESULTS AND DISCUSSION**

Table 2 shows the results for quality control using a standard reference material, NIST 1633b. The results presented indicate that the concentrations of most of the elements, within the limit of experimental errors agree reasonably well with the certified (literature) values. This justifies the analytical technique used in terms of accuracy.

 Element	Certified values	This work
 Al (%)	$15.05\pm0.27$	$13.45 \pm 0.09$
As	$136.20\pm2.60$	$136.00 \pm 70.00$
Ba	$709.00\pm27.00$	$709.00\pm50.00$
Ca (%)	$1.51\pm0.06$	$1.50\pm0.39$
Со	-	$50.00\pm2.00$
Cr	$198.20\pm4.70$	$198.00\pm8.00$
Cs	-	$11.00 \pm 1.00$
Dy	-	$13.40\pm0.40$
Eu	-	$4.10\pm0.30$
Fe (%)	$7.78\pm0.23$	$7.78\pm0.08$
Hf	-	$6.80\pm0.10$
K (%)	$1.95\pm0.03$	$1.95\pm0.02$
La	-	$94.0\pm0.30$
Lu	-	$1.20\pm0.06$
Mg (%)	0.48	$0.46\pm0.10$
Mn	$131.80\pm1.70$	$123.40 \pm 1.00$
Na (%)	$0.20\pm0.00$	$0.201\pm0.00$
Rb	-	$140.00\pm8.00$
Sc	-	$41.00\pm0.40$
Та	-	$1.80 \pm 0.20$
Th	$25.70 \pm 1.30$	$25.70\pm0.30$
Ti (%)	$0.791 \pm 0.014$	$0.39\pm0.04$
V	$295.70\pm3.60$	$265.00 \pm 8.00$
Yb	-	$7.60 \pm 0.40$
Zn	-	$210.00 \pm 36.00$

Table 2. Quality Control using Coal Fly-Ash (NIST 1633b)(in µg/g or in % as specified)

Target	Product	Half-life	Gamma energy
lsotope	isotope (n,γ)	$(T_{1/2})$	(keV)
<sup>23</sup> Na	<sup>24</sup> Na	14.96 h	1368.60
<sup>26</sup> Mg	<sup>27</sup> Mg	9.46 min	1014.40
<sup>27</sup> Al	<sup>28</sup> Al	2.24 min	1778.99
<sup>41</sup> K	$^{42}$ K	12.36 h	1524.58
<sup>45</sup> Sc	<sup>46</sup> Sc	83.81 d	889.28
<sup>48</sup> Ca	<sup>49</sup> Ca	8.72 min	3084.54
<sup>50</sup> Ti	<sup>51</sup> Ti	5.76 min	320.08
<sup>50</sup> Cr	<sup>51</sup> Cr	27.70 d	320.98
<sup>51</sup> V	$^{52}$ V	3.75 min	1434.08
<sup>55</sup> Mn	<sup>56</sup> Mn	2.58 h	846.76
<sup>58</sup> Fe	<sup>59</sup> Fe	44.50 d	1099.25
<sup>59</sup> Co	<sup>60</sup> Co	5.27 y	1173.20
<sup>64</sup> Zn	<sup>65</sup> Zn	243.90 d	1115.55
<sup>75</sup> As	<sup>76</sup> As	26.32 h	559.10
<sup>85</sup> Rb	<sup>86</sup> Rb	18.80 d	1076.60
<sup>130</sup> Ba	<sup>131</sup> Ba	11.80 d	496.30
<sup>133</sup> Cs	<sup>134</sup> Cs	2.06 y	795.85
<sup>139</sup> La	$^{140}$ La	40.30 h	1596.21
<sup>151</sup> Eu	<sup>152</sup> Eu	13.30 y	1408.50
<sup>164</sup> Dy	<sup>165</sup> Dy	2.33 h	94.70
<sup>174</sup> Yb	<sup>175</sup> Yb	4.19 d	396.33
<sup>176</sup> Lu	<sup>177</sup> Lu	6.71 d	208.36
<sup>180</sup> Hf	<sup>181</sup> Hf	42.40 d	482.20
<sup>181</sup> Ta	<sup>182</sup> Ta	115.00 d	1221.40
<sup>232</sup> Th	<sup>233</sup> Pa	27.00 đ	312.01

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Tables 1 and 3 present the irradiation and counting schemes used for this study, and the nuclear data for the elements of interest respectively. Table 4 reveals that a total of 25 elements (Mg, Al, Ti, V, Mn, Na, K, As, La, Sc, Cr, Fe, Co, Zn, Rb, Sb, Cs, Ba, Eu, Yb, Lu, Hf, Ta, Th, and Dy) were detected in concentrations ranging from 1.72  $\mu$ g/g (Ta) to 5.6 % (Fe) in soil, 1.50

(Ta) to 6.6% (Fe) in sediments, and the concentrations of the elements in the background ranged from 0.17 µg/g (Lu) to 5.50 % (Fe). Table 5 on the other hand gives the background loading factors of all the elements detected. These results revealed that the concentrations of the elements were generally higher in the agricultural soils and the sediments than the background levels. Results from similar work carried out by [10] are in good agreement with those in the work being reported here, though they employed the technique of atomic absorption spectrometry and very few elements were determined. Our work also revealed higher metal concentrations in soil compared to those reported by [11] and in both soils and sediments relative to [12]. Five unique elements known as the rare earth elements (including La, Dy, Yb, Lu, and Eu) were identified. The rare earth plots [13] further validate the results of this work as the plots show consistency with rare earth patterns [14, 15]. All elements listed were detected in both the terrestrial (soils) and aquatic (sediments) environments. They belong to the groups of elements known as the major elements (K, Al, Fe, Mg, and Ti); minor elements (Na, Ba, and Mn); and trace elements (Co, Cr, Eu, Hf, La, Th, Rb, Sb, V, Sc, Lu, Yb, Cs, Ta, Zn, Dy, and As).

On Table 4 it is obvious that Al, Ba, Hf, K, Mn, Na, Rb, Ta, Th, V, Ti, and Ta showed various levels of enrichment in the aquatic sediments as compared to results of the soils. The reason for the depletion was not quite obvious, but could be attributed to increase in the leaching of elements which have their sources from composite fractions in the natural geochemistry of the upstream detrital and the run-offs from the upland soils. The observed enrichment of some major elements (Fe, Mg, and Ti) in the agricultural soils could be attributed to activities such as the application of pesticides, herbicides [16] and fertilizers (for the purpose of soil enrichment) by farmers. Dumping of refuse that accrued from sundry activities around the refinery upstream could also have played significant roles in the build-up in the sediments. Surface run-offs during the rainy seasons could also have drained these detrital into the river bed aided by gravitational impactions. The presence of Fe in substantial amounts (5.26 %) in this study is suggestive of the presence of iron-rich minerals responsible for the hard-pan concretions during the dry seasons [17].

 Element	Soils (SD)	Sediments (SD)	Mean Bg (SD)
 Al(%)	5.26(0.10)	4.71(0.00)	5.50(0.10)
As	47.05(2.00)	100.80(5.60)	4.80(0.20)
Ba	223.90(29.50)	232.20(41.60)	721.20(41.50)
Со	30.77(0.90)	39.60(1.80)	15.20(0.40)
Cr	162.95(4.40)	155.00(6.60)	74.00(3.00)
Cs	5.62(0.60)	9.60(1.00)	3.75(0.30)
Dy	7.33(0.30)	45.20(2.00)	5.85(0.70)
Eu	6.08(0.20)	3.60(0.34)	1.32(0.10)
Fe(%)	5.56(0.04)	6.60(0.06)	5.31(0.04)
Hf	15.43(0.30)	5.20(0.09)	23.00(0.40)
K(%)	0.58(0.02)	0.27(0.01)	2.28(0.03)
La	76.56(0.33)	104.80(0.30)	54.55(0.20)
Lu	6.91(0.20)	1.60(0.09)	0.70(0.04)
Mg(%)	0.46(0.11)	0.53(0.14)	0.20(0.05)
Mn	361.40(2.20)	313.00(4.20)	770.00(30.00)
Na(%)	0.05(0.01)	0.04(0.00)	0.17(0.00)
Rb	76.17(7.50)	63.80(4.00)	113.50(6.50)
Sb	2.74(0.50)	7.30(1.50)	0.56(0.20)
Sc	27.68(0.30)	47.10(1.10)	6.16(0.10)
Та	1.72(0.20)	1.50(0.10)	2.20(0.20)
Th	20.25(0.30)	25.70(0.30)	24.65(0.30)
Ti(%)	0.39(0.04)	0.62(0.04)	0.43(0.040)
V	76.96(4.60)	66.40(4.20)	105.00(5.50)
Yb	9.10(0.30)	12.80(0.50)	2.75(0.20)
Zn	146.69(13.40)	464.70(29.70)	26.00(4.50)

Table 4. Major, Minor, and Trace Elements in Soils and Sediments (All units are in  $\mu g/g$  unless as otherwise stated)

Table 5. Background Loading Factor (BLF)			
 Element	Mean Bg	BLF	
Al(%)	54740.0	0.96	
As	4.8	9.80	
Ba	721.2	0.31	
Co	15.2	2.02	
Cr	74.0	2.20	
Cs	3.8	1.5	
Dy	5.9	1.25	
Eu	1.3	4.61	
Fe(%)	5.31	1.05	
Hf	23.0	0.67	
K(%)	2.28	0.25	
La	54.6	1.40	
Lu	0.7	9.87	
Mg(%)	2.03	2.28	
Mn	770.0	0.47	
Na(%)	1.72	0.31	
Rb	113.5	0.67	
Sb	0.6	4.89	
Sc	6.2	4.49	
Та	2.2	0.78	
Th	24.7	0.82	
Ti(%)	4.31	0.91	
V	1.0.0	0.73	
Yb	2.8	3.31	
Zn	26.0	5.64	

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### CONCLUSION

INAA was used to identify 25 (major, minor, and trace) elements in soil and sediments around the refinery including five rare earth elements (REE). The elements were determined in concentrations which ranged between 1.72  $\mu$ g/g (Ta) to 5.56 % (Fe). Measurements and observations have revealed that the environment of Kaduna Refinery is polluted with elevated levels of trace elements. About 56 % occurred above the background levels with background loading factor (BLF) reaching as high as 9.87 (Lu). The elevated levels of the metals can however be attributed to applications of phosphate fertilizers, pesticides, herbicides, and wastes from associated activities around the refinery complex.

#### REFERENCES

- [1] Dambo, W. B. (2000): Ecotoxicology of Heavy Metals and Petroleum Compounds on the Mangrove Oysters from the Lower Bonny Estuary. Unpublished PhD Dissertation, Rivers State University of Science and Technology, Port Harcourt.
- [2] Mogo, F. G., (2002). Assessment of Heavy Metals in Soil, Water, Sediments and Certain Plant Taxa in Imo State and New Calabar Rivers. Unpublished PhD Dissertation, University of Port Harcourt, Nigeria.
- [3] Ravenswaay, E. O. V. (1998). EEP 255: Pollution Prevention Case Study on Petroleum Refining (in) USEPA Profile of the Petroleum Refining Industry, EPA 310-R-95-013.
- [4] Jonah, S. A., Williams, I. S., Nyarko, B. J. B., Akaho, E. H. K., & Serfor-Armah, Y. (2003). Routine Monitoring of Market Infant Foods by Neutron Activation Analysis with a Low-Power Reactor. *Journal of Trace and Microprobe techniques*, 21(2), 407 – 413 Doi: 10.1081/TMA-120020275
- [5] Ewa, I. O. B. (2004). Data evaluation of trace elements determined in Nigerian Coal using cluster procedures. *Applied Radiation and Isotopes*, 60, 751 758. Doi: 10.1016/j.apradiso.2003.10.002
- [6] Jonah, S.A., Umar, I. M., Oladipo, M.O.A., Balogun, G.I. & Adeyemo D.J. (2006).
   Standardization of NIRR-1 irradiation and counting facilities for Instrumental neutron activation Analysis. *Applied Radiation and Isotopes*, 64, 818- 822.Doi: 10.1016/j.apradiso.2006.01.012
- [7] Glascock, M. D. (2005). Overview of Neutron Activation Analysis. University of Missouri Research Reactor Center, Columbia, MO.

- [8] Akaho E. H. K. & Nyarko, B. J. B. (2002). Characterization of Neutron Flux Spectra in Irradiation Sites of MNSR Reactor using the Westcott-formalism for the k<sub>0</sub> Neutron Activation Analysis Method. *Applied Radiation and Isotopes*, 57, 265 – 273.
- [9] Jonah, S. A., Balogun, G. I. Umar, I. M. & Mayaki, M. C. (2005). Neutron Spectrum Parameters in Standardization. *Journal of Radioanalytical and Nuclear Chemistry*, 206 (1), 83 – 88.
- [10] Ndiokwere, C. L. & Ezihe, C. A. (1990). The Occurrence of Heavy Metals in the Vicinity of Industrial Complexes in Nigeria. *Environment International*, 16, 291 - 295
- [11] Bukar, P. H. (2016). Assessment of the Distribution of Trace Elements in Soil and Vegetables cultivated along River Ngadda and Alau Dam in Maiduguri, Borno State. Unpublished Ph.D Dissertation, Ahmadu Bello University, Zaria
- [12] Ewa, I. O. B., Oladipo, M. O. A. & Umar, I. M. (2005). Trace Element Levels in Terrestrial and Aquatic Environments Near the Nigeria Research Reactor. *Journal of Environmental Systems*, 32(1), 17 – 26, doi: 10.2190/ES.32.1.c
- [13] Onoja, M. A., Ewa, I. O. B., Oladipo, M. O. A. & Kassimu, A. A. (2018). Rare Earth Elements Patterns in Soil around Kaduna Refinery, Kaduna State, Nigeria. *Journal of Science, Technology and Mathematics Education (JOSTMED),* 14(1): 13 – 19. Published by the Department of Science Education, Federal University of Technology, Minna, Nigeria, Africa.
- [14] Ewa, I. O. B., Elegba, S. B. & Adetunji, J. (1996). Rare Earth Element Patterns in Nigerian Coals. *Journal of Radioanalytical and Nuclear Chemistry, Letters*, 213(3), 213 – 224
- [15] Haskin, L. A. (1984). In: Henderson, P. (Ed.). Rare Earth Element Geochemistry, Elsevier, Amsterdam
- [16] Onoja, M. A. & Ibeanu, I. G. E. (2015). Application of EDXRF in the Determination of the Abundance and Distribution of Arsenic along a Federal Highway in Northern Nigeria.
   *Physical Science International Journal*, 8(2), 1 9, Article no.PSIJ.6789, *Science domain international*, USA UK INDIA
- [17] Ewa, I. O. B., Oladipo, M. O. A., Dim, L. A. & Mallam, S. P. (2000). Major, minor and trace elements of the Samaru savannah soil in Nigeria. *Journal of trace and microprobe techniques*, 18(3), 389 - 395