International Journal of Research
Available at https://edupediapublications.org/journals
p-ISSN: 2348-6848
e-ISSN: 2348-795X
Volume 03 Issue 09
May 2016

Elemental Analysis of Soil around Ikot Abasi L.G.A, Nigeria Using Edxrf.

***Essiett, A. A., & Bede, M. C.**

Department Of Physics, University Of Uyo, Uyo - Nigeria .
Corresponding: Author Email: aessiett2@yahoo.com

ABSTRACT
Elemental analysis of soil around Ikot Abasi L.G.A Nigeria was carried out using Energy Dispersive X-ray Fluorescence (EDXRF). The EDXRF technique was capable of detecting the presence of fourteen elements (K, Ca, Ti, V, Mn, Fe, Co, Zn, Pb, Br, Sr, Zr, Nb and Mo). The concentration of Pb in the soil ranged from 58.200 – 85.300 ppm, while Zn ranged from 19,000 – 181,000 ppm. Analysis of the result of EDXRF technique showed that Sr is depleted in the soil with respect to the normalized Clarke value, while K, Ti, Co, Zn and Nb were enriched. The enrichment factors ranged from 1-45.
Keywords: EDXRF; Clarke value; Enrichment factors; Soil.

INTRODUCTION

The state of the contamination of our environment has an overwhelming effect on the quality of human health. Soil pollution is one of the most serious problems in the world, with long term consequences on human life. Heavy metals and some trace elements are biologically toxic and can affect and threaten the health of human being owing to their accumulation and persistence in the compartments of the food chain. Thus, it is very important to investigate and monitor soil contamination for economic sustainable development and people's health. EDXRF has the advantage of being a rapid and inexpensive method with a simple sample preparation (Cojocaru *et al.*, 2006, Ene *et al.*, 2010 and EPA, 2006). Enrichment Factor is a ratio between elemental concentration, and widely applied in several pollution related studies, to distinguish between possible sources of pollutants either in soil, deposition aerosols, or sediments samples (Adejumo *et al.*,1994, Asubiojo *et al.*,1993 and Vermette *et al.*,1988). According to Galloway(1982) if an Enrichment factor (EF) is greater than one; such element is considered to be enriched relative to its concentration in the earth crust. That is, such elements have other sources other than the earth crust. If the EF is equal to one then the element under investigation is not enriched in the atmosphere, implying a crustal source. A value of EF which is equal to or greater than ten is considered highly enriched. The main objective of this work was to use EDXRF technique to determine the current baseline of soil within Ikot Abasi L.G.A. of Akwa Ibom State.

MATERIALS AND METHODS

Surface soil (0-5 cm depth) was collected at each sample location. The quartered samples were ground manually to powder with an agate mortar and pestle to grain size of less than 125µm. pellets of 19mm diameter were prepared from 0.3 – 0.5 g powder mixed with three drops of organic liquid binder and pressed afterwards at 10 tons with a hydraulic press. Measurements were performed using an annular 25 mci ^{109}Cd as the excitation source, that emits Ag-K X-rays

(22.1 keV) in which case all elements with lower characteristic excitation energies were accessible for detection in the samples. The system consists of a Si (Li) detector, with a resolution of 170 eV for the 5.90 keV line, coupled to a computer controlled ADC-card. Quantitative analysis by modified version of Emission Transmission (E-T) method (Angeyo *et al.*,1998, Funtua, 1999a and Funtua, 1999b) was employed and it involves the use of pure target material (Mo) to measure the absorption factors in the sample. The Mo target serves as a source of monochromatic X-rays, which are excited through the sample by primary radiation and then penetrate the sample on the way to the detector. In this way, the absorption factor is experimentally determined which the program uses in the quantification of concentration of the elements. In addition, the contribution to the Mo – K peak intensity by the Zr – K is subtracted for each sample. Sensitivity calibration of the system was performed using thick pure metal foils (Ti, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Sn, Ta, Pb) and stable chemical compounds (K_2CO_3, $CaCO_3$, Ce_2O_3, WO_3, ThO_2, U_3O_8). The spectra for the samples were collected for 3000 s with the ^{109}Cd source and 2000 s for the ^{55}Fe source and the spectra were then evaluated using the AXIL – QXAS program (Bernasconi *et al.*,1996).

Two certified standard reference materials namely NIST 688 and USGS – AGVI, were used for quality control in this work. Pellets of these certified reference materials were irradiated by ^{55}Fe and ^{109}Cd sources and their characteristic X-rays analyzed in the same way as the soil samples described. The results are given in Table 1and Table 2. Clarke ratio is defined as the ratio of concentration of element of in the sample to the mean global concentration of the same element in the earth's crust. It shows the magnitude of the variation of an element in a given location with respect to a geochemically accepted and globally fixed value called 'Clarke Value'.

Clarke Ratio is defined thus:

$$R = \left[X_s \Big/ X_c \right] 100$$

Where X_s is the concentration of element in sample

X_c is the Clarke Value for the given element.

RESULTS AND DISCUSSION

The result of the elemental composition analysis of the soil samples around Ikot Abasi using EDXRF technique is presented in Table 1. A total of fourteen elements have been determined in the soil samples using the EDXRF technique. The elements analyzed include halogen element and heavy metals such as Pb and Zn. These elements are of particular interest from transportation (automotive) pollution considerations. Pb is generally considered a marker elements for industrial pollution while Br is one of the marker elements for marine contribution. The observed Pb concentration of 85.3 ppm was obtained at one of the transportation locations. Ndiokwere (1984) determined the Pb concentration in soils along Benin-Onitsha highway to be 247.0 µkg/g. In this work, Zn is uniformly is distributed in all the soil sample around Ikot Abasi ALSCON plant, apart from one of the commercial locations where a value of 287.0 ppm was obtained. The EDXRF technique also revealed the presence of Sr, Zr, Nb and Mo in soil samples. Table 1 shows high level of Zirconium concentration in the soil

samples at all the designated sites with a range of 140-289 ppm. According to Bowen (1979) Zirconium is lethal to rats at the level of 250-700 mg/day, while Niobium is moderately toxic to mammals, at a level above 33 ppm.

Enrichment factors of some of the elements were determined for all the soil samples collected around the Ikot Abasi Smelter plant (Table 2). The enrichment factor is always compared with the Clarke values of the element in the earth's crust. Clarke values as proposed by Fortescue (1992) were used to determined the Enrichment Factors in the soil around the Ikot Abasi ALSCON Plant. Mean values of Crustal Enrichment Factors for the soil around the ALSCON Plant are shown in Table 5. From the table, it is seen that only one element, Sr is depleted with respect to the normalized Clarke value of Fortescue (1992). All the other elements, K, Ti, Co, Zn and Nb were enriched with factors ranging between 1 and 45. The depleted element could either suggest absence of periodic contamination or dilution of the meal complexes in which it exists in the soil. The most enriched element in the soil around the Ikot Abasi Aluminium Smelter Plant is cobalt with factor ranging between 40.639 and 57.090 in all the designated locations (Table 2). Summary of Clarke Enrichment Factors (EF) of the soil around the Ikot Abasi Aluminium Smelter Plant is presented in Table 5.

Table 2 shows that Ca is not enriched while K, Ti, Zn and Nb are moderately enriched. Elements like Zn and Nb with enrichment factors between 1 and 10 are known to be toxic to some extent (Bowen, 1979). Titanium and Calcium are known to be harmless to all organisms (Bowen, 1979). Element like Co is known to be very toxic to plants. Zinc is the element most frequently associated with plant damage from industrial emissions, example near smelters, on mine wastes, sludge, river dredging, and near galvanized steel buildings (Patterson, 1971; Barrrow and Weber, 1972).

Table 6 shows the Clarke Ratio for some trace elements in soils around Ikot Abasi ALSCON Plant. The Clarke Ratio shows that the following elements K, Ca, Ti, Fe, Nb and Sr were enriched (Table 5), while Co and Zn are highly enriched as we have seen in the case of enrichment factors. This suggests that iron is a good normalizing element, as the enrichment factors are in agreement with the Clarke Ratio results

The quality assurance for the EDXRF was done using two certified reference materials, NIST 688 and USGS – AGVI. The results are shown in Table 3 and Table 4. Most of the elements measured are in good agreement with the certified values. The quality assurance results also show that the technique is better than 5% for most of the elements.

TABLE 1: RESULTS OF ELEMENTAL ANALYSIS OF SOIL IN IKOT ABASI USING EDXRF (VALUES IN PPM OTHERWISE AS SPECIFIED)

Element	SOKTS01	SOKTS02	SOKTS03	SOKTS04	SOKTS05	SOETE01	SOSEN01	SOAYA01	SOKWA01	SOKON01
K (%)	1.690	1.880	1.760	1.690	1.800	1.650	1.640	1.700	1.890	1.760
Ca (%)	1.370	1.420	1.740	1.080	1.120	1.450	1.080	1.780	1.190	1.330
Ti (%)	0.498	0.311	0.474	0.420	0.731	0.327	0.622	0.622	0.586	0.520
V	2450.000	1910.00	1930.000	1460.000	1520.00	1440.000	1420.000	1420.000	1670.000	1610.000
Mn	1350.000	609.000	617.000	582.000	591.000	637.000	589.000	589.000	718.000	640.000
Fe	1.820	0.938	1.160	1.990	1.870	0.923	1.490	1.990	1.260	2.190

Co	308.000	296.000	297.000	332.000	360.000	310.000	326.000	416.000	343.000	322.000
Zn	88.300	181.000	97.400	87.400	108.000	287.000	87.100	125.000	19.000	118.000
Pb	61.100	58.200	63.100	58.500	58.900	72.100	85.300	71.000	63.100	68.200
Br	24.900	23.900	28.600	24.300	26.300	25.800	23.900	25.400	31.700	32.800
Sr	24.000	44.000	19.300	19.100	30.000	22.800	18.000	25.600	30.500	24.500
Zr	289.000	140.000	351.000	274.000	226.000	228.000	263.000	428.000	380.000	275.000
Nb	18.300	11.900	14.500	18.400	15.400	19.100	16.300	18.400	13.600	17.800
Mo	12.500	13.000	11.000	11.700	11.500	12.400	12.800	12.900	14.200	16.900

Error using one standard deviation is ±√net count.

TABLE 2: CRUSTAL ENRICHMENT FACTORS (CEFS) OF SOME TRACE ELEMENTS IN SOILS AROUND IKOT ABASI ALUMINIUM SMELTING PLANT

Element	SOKTS01	SOKTS02	SOKTS03	SOKTS04	SOKTS05	SOETE01	SOSEN01	SOAYA01	SOKWA01	SOKON01
K	3.652	4.064	3.804	3.653	3.891	3.567	3.545	3.675	4.085	3.804
Ca	1.170	1.213	1.486	0.923	0.923	1.521	0.923	1.521	1.017	1.136
Ti	3.124	1.951	2.973	2.635	3.902	3.914	3.902	3.914	3.676	3.262
Co	42.269	40.639	40.759	45.562	44.739	57.090	44.739	57.090	47.072	44.190
Zn	4.624	9.477	5.100	4.576	4.561	6.545	15.028	6.545	6.231	6.179
Sr	0.249	0.456	0.200	0.198	0.187	0.265	0.236	0.265	0.316	0.254
Nb	3.647	2.368	2.886	3.662	3.244	3.662	3.801	3.662	2.706	3.542

TABLE 3: RESULT OF ELEMENTAL CONTENT OF CERTIFIED STANDARD REFERENCE MATERIAL, USGS – AGVI USING EDXRF (VALUES IN PPM OTHERWISE, AS SPECIFIED)

Elements	Certified value	This work
Si %	27.4	25.1
K %	2.41	2.50
Ca %	3.53	3.72
Ti %	0.63	0.68
V	121.0	140.0
Fe	1.60	1.60
Co	15.3	-
Zn	88.0	-
Rb	67.3	51.2
Sr	662.0	651.0
Y	20.0	16.4
Zr	227.0	227.0
Nb	15.0	-

TABLE 4: RESULT OF ELEMENTAL CONTENT OF CERTIFIED STANDARD REFERENCE MATERIAL, NIST 688 USING EDXRF (VALUES IN PPM OTHERWISE, AS SPECIFIED)

Elements	Certified value	This work
Si %	22.5	25.5
K %	0.16	0.06
Ca %	8.68	8.45
Ti %	0.70	0.67

V	250	2.25
Fe	5.93	2.24
Co	49.7	49.7
Zn	58.0	-
Rb	1.91	ND
Sr	169.0	163.5
Y	17.0	16.4
Zr	60.6	60.6
Nb	ND	-

TABLE 5: SUMMARY OF THE CLARKE RATIO FOR SOIL AROUND THE IKOT ABASI ALSCON PLANT

Clarke Ratio Ranges (R)	Elements
R < 10	-
10 < R < 100	K, Ca, Ti, Fe, Nb, Sr
100 < R < 1500	Co, Zn

TABLE 6: CLARKE RATIO FOR SOME TRACE ELEMENTS IN SOILS AROUND IKOT ABASI ALUMINIUM SMELTING PLANT

Element	SOKTS01	SOKTS02	SOKTS03	SOKTS04	SOKTS05	SOETE01	SOSEN01	SOAYA01	SOKWA01	SOKON01
K	91.848	102.174	95.652	91.848	97.826	89.674	89.130	92.391	102.717	95.652
Ca	29.399	30.472	37.339	23.176	24.034	31.112	23.176	38.197	25.537	28.541
Ti	78.798	49.209	75.000	66.456	115.665	57.741	98.418	98.734	92.722	82.279
Fe	190.032	15.080	18.650	29.880	30.161	14.839	23.955	31.994	20.257	35.209
Co	1062.069	1020.689	1024.138	14.828	1241.379	1068.966	1434.482	1434.483	1182.759	1110.345
Zn	116.184	238.158	128.158	115.000	142.105	377.630	14.605	164.474	156.579	155.263
Sr	25.260	11.458	11.458	4.934	7.813	5.938	4.688	6.667	7.943	6.380
Nb	91.500	59.500	59.500	92.000	77.000	95.500	81.500	92.000	68.000	89.000

CONCLUSION

The EDXRF technique was capable of detecting the presence of fourteen elements (K, Ca, Ti, V, Mn, Fe, Co, Zn, Pb, Br, Sr, Zr, Nb and Mo). This technique has been able to determine the presence of Pb and Zn in the soil, which could not be detected by INAA technique. The concentration of Pb in the soil ranged from 58.200 – 85.300 ppm, while Zn ranged from 19,000 – 181,000 ppm. Geochemical analysis of the result of EDXRF technique shows that Sr is depleted in the soil with respect to the normalized Clarke Value, while K, Ti, Co, Zn and Nb were enriched. The enrichment factor ranged from 1 – 45, the depleted element in the soil around the ALSCON Plant, could either suggest absence of periodic contamination or dilution of the metal complexes in which it exist in the soil. Cobalt is the most enriched element in the soil around the Ikot Abasi Aluminium smelter Plant with a factor from 41 – 57 in the sample analyzed. The Clarke ratio shows that K, Ca, Ti, Fe, Nb and Sr were moderately enriched, while Co and Zn were highly enriched. The result obtained from this work therefore provides the baseline data for future studies in Ikot Abasi Local Government Area.

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