Elemental Characterization of Soils Collected From Mining Sites in Anka Local Government Area Zamfara State, Northwest Nigeria by Instrumental Thermal and Epithermal Neutron Activation Analysis

C.P Egwuogu[1], M.O.A Oladipo[2]

[1]Nigeria Atomic Energy Commission, Abuja, Nigeria
[2]Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria

Abstract:- **Elemental concentration of Fifteen samples representatively collected from three different mining sites: Bagega, Dareta and Sunke in Anka LGA, Zamfara state, Nigeria were determined using Instrumental Thermal and Epithermal Neutron activation analysis available on NIRR-1 at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria. Quality control of the work was assured by analyzing an international standard reference material, NIST 1633b using the same scheme employed in this investigation. A baseline of 34 elements were found and established. Ten elements; Si, Fe, Ba, Sb, Ti, Al, K, Ca, Mg and Na showed concentrations above 1000ppm (μgg^{-1}) in most of the samples. Most of the trace elements were present in concentrations within the Maximum Allowable Concentration (MAC) of various countries.**

Keywords: **ITNAA, IENAA, Trace elements**

I. INTRODUCTION

Zamfara is a Statein northwest Nigeria endowed with solid minerals, chief among is gold. Mining of this mineral have been going on for decades in the state, although illegally and unregulated (Momoh, 2013), attention was not drawn to Zamfara state until the Lead (Pb) pollution crisis of 2010 in the State (Dooyema et al, 2010). However, there are other elements, in addition to lead, that are associated with gold in its natural geochemical setting. After mining the gold, these other elements are discarded as wastes into the environment.Serious health hazards are posed to host communities with elevated concentrations of these elements in the water bodies. Human health is threatened when these metal contaminants migrate and contaminate soils, streams, groundwater, and crops (Ramani, 2001). The dangerous possibility may occur such as contamination of the crop (in terms of heavy metal uptake by the plant), pollution of underground water, influence the plant growth and make the soil generally considered toxic. It becomes pertinent that the elements present in the Bagega, Dareta and Sunke mining sites be analyzed and their concentration determined and assessed to ascertain whether they lie within a safe level. This paper, therefore focuses on the;

i. Determination of the elements and the concentration released into the environment from the depth of the earth as a result of the gold mining activities carried out in Bagega, Dareta and Sunke in Anka Local Government Area.
ii. Determination of other heavy metals asides Pb present and the level in which they are present.

To determine the elements released into the environment as a result of the mining activities going on in these areas, highly sensitive and element specific analytical techniques are needed. Neutron Activation Analysis being a multielemental analytical technique involving the use of thermal and epithermal neutrons as activating particles appears to be suitable for this investigation.

II. EXPERIMENTAL

2.1 Sample collection and preparation

The study was conducted over some mining sites/environment in Zamfara State within which fifteen study sites were chosen. The locations are as listed in Table 1. The choice of sampling locations was based on mining areas where there were incidences of Pb poisoning of infants. From the three study areas, Bagega, Dareta and Sunke, fifteen different samples were collected.One to two kg of sample was taken at each site. Four of the fifteen samples were collected from Bagega mining site; Eight samples including an out- crop sample were collected from Dareta and the remaining three samples from Sunke. Samples of soil or sediment were collected from freshly dug mining pits, washing points or in some cases by clearing the surface vegetation from a location after which a core sample was taken manually.Sample of soil used for remediation was collected at Dareta to serve as a control. These samples were bulked separately in plastic bags and sealed and then transported to the laboratory for further treatment.

To prepare the samples for analysis, each sample was thoroughly dried at room temperature and then inside an oven preset at 60^oC until a consistent dry weight was obtained. The

samples were crushed and ground into powder .About 200mg of the homogenized samples were weighed into a pre-cleaned polyethylene container, sealed and labeled, ready for transfer into aluminum cans for irradiation. The quality control standards; NIST 1633b used for thermal instrumental neutron activation analysis and NIST 1633a Coal Fly Ash for the epithermal neutron activation analysis were also prepared in a similar manner.

Table 1 shows the locations where the samples for analysis were taken from and the laboratory codes assigned to each of them.

Table 1: Locations at which soil samples were taken

S/N	Laboratory Codes	Location Description
1	BW5	Tailings collected from Washing Point I at Bagega
2	BW6	Tailings collected from Washing Point II at Bagega
3	DSD14	Supposedly contaminated soil Samples collected at Dareta
4	BB7	Sample was collected from Bagega(basin-like) representing wash-offs
5	BS10	Sample collected from the washing bed at Bagega
6	DM12	The mined outcrop from Dareta
7	SM4	Sample from Mining Site in Sunke-flooded area but now dry
8	SF8	Soil sample from Sunke flood area II
9	SF9	Soil sample from Sunke flood area III
10	DSR13	Uncontaminated soil used in the remediation work at Dareta
11	DSW15	Soil collected from a washing point I (red soil) in Dareta
12	DS11	Soil collected from washing point II in Dareta
13	DMW1	Crushed mine wastes collected at Dareta
14	DR2	Sample collected from a rig well at Dareta
15	DD3	Mineral Debris collected at Dareta mining site

2.2 Irradiation

The research reactor, 30 kW Nigeria research reactor 1 (NIRR-1) situated at the centre for energy, research and training (CERT), Ahmadu Bello University, Zaria was used for irradiation. The NIRR-1 has 10 irradiation sites (5 small inner, 3 small outer and 2 large outer). The 5 small inner irradiation sites are for Thermal neutron activation analysis (TNAA). Majority of the elements could be detected using TNAA. However silicon, which is an important element in soil lies in the fast region of the reactor neutron spectrum. To be able to detect Si, the capability of the NIRR-1 was further exploited through the Epithermal neutron activation analysis (ENAA). This is possible because even though Si lies in the fast region, its high concentration in soils enables it to be determined using ENAA.

For short-lived irradiations, designed to capture short half-lives radionuclide the samples were place directly into the irradiation tube at the outer irradiation channels (B4, A2) at a flux of 1×10^{11} ncm^{-2} s^{-1}. Multielement standards were employed and prepared as unknown samples. The thermal short irradiation was carried out in two regimes; S1 and S2. For S1, samples were irradiated for 2mins, cooled (allowed to decay) for 15mins before being measured for 10mins. For S2, samples were irradiated for 2mins, cooled for 4hrs before being measured for 10mins.For thermal/epithermal short-lived irradiations, samples and standards were irradiated simultaneously.

For the thermal long-lived irradiations, however, samples and standards were enclosed in an irradiation tube which usually would take six samples and two multielement standards and irradiated at a flux of 5×10^{11} ncm^{-2} s^{-1} at the inner irradiation channels (B1, B2, B3, and A1). The thermal long- lived irradiation was also in two regimes; L1 and L2. For L1,samples were irradiated for 6hrs, cooled for 5days before being measured for 30mins. For L2, samples were irradiated for 6hrs, cooled for 15days before being measured for 60mins.

For the epithermal irradiation carried out at a neutron flux of 8×10^{11} $ncm^{-2}s^{-1}$ at outer irradiation channel A3, only the short irradiation was done and this was also in two regimes S1 and S2. For S1,samples were irradiated for 10mins, cooled for 17mins before being measured for 10 mins. For S2, samples were irradiated for 10mins, cooled for 280mins before being measured for 10mins.The larger outer irradiation channel A3 has a permanent cadmium(Cd) lining of thickness 1.0mm and length 250.00mm. The Cd cut off thermal neutrons completely from the neutron spectrum available in the epithermal channel of NIRR-1 research reactor.

2.3 Gamma ray spectrum measurement

Measurement of induced radioactivity which is a an important step of every INAA procedure was done by gamma- ray spectrometry using a high purity germanium detector calibrated using ^{137}Cs (661.6 KeV) and ^{60}Co (1173 KeV and 1332.5 KeV) sealed standard radioactive source. Sufficient activity from both sources was acquired and the channel numbers i.e. the positions on the energy/channel axis of the spectrum versus the intensity of the following gamma energies 661.6 KeV and 1332.5 KeV was used for calibration. The expected three gamma rays were seen appearing in the spectrum after the rays were acquired (or measured) for some time. The second peak of ^{60}Co at 1173 KeV was used in confirming the accuracy of the calibration procedure.(Jonah et al, 2006).

Following the short irradiation regime, for thermal NAA, the first round of counting is performed for 10mins.Samples were placed on a plexi-glass sample holder designated as "H2" which corresponds to a source- detector geometry of 5cm. The second round of counting also carried out for 10mins, samples were placed on a plexi-glass sample holder designated as "H1" which corresponds to a source- detector geometry of 1cm.

For the long irradiation regime, the first round of counting is carried out for 30mins, following the long irradiation (L1) using the holder "H1". The second round of counting is performed for 60mins (L2).

For the ENAA short irradiation regime, the first round of counting is performed for 10mins (S1) with samples placed on a plexi-glass sample holder designated as "H2" which corresponds to a source- detector geometry of 5 cm. The second round of counting was also carried out for 10mins, following the short irradiation regime (S2) and samples were placed on a plexi-glass sample holder designated as "H1" which corresponds to a source- detector geometry of 1cm.

III. DISCUSSION OF RESULTS

3.1 Result of the standards

Analysis of results must commence with reliability check of the procedure employed in the work. This is similarly known as quality control. NIST- produced international standard, NIST 1633b and NIST 1633a were irradiated and counted using the same set of conditions as the unknown samples investigated in this work. The results obtained are as shown in Table 2.

Table 2: Results of the elemental abundances of NIST 1633b as a quality control for the analysis

Element	Certified Values (Rocio et al ,2004) (ppm)	Values obtained in this work (ppm)
Al	150500 ± 2700	150500 ±1500
Ca	15100 ± 600	15100 ± 1800
Fe	77800 ± 2300	78400 ± 500
Mg	4820 ± 80	4820 ± 700
K	19500 ± 300	19300 ± 300
Na	2010 ± 300	1950 ± 6
Ti	7910 ± 410	7910 ± 450
As	136.2 ± 2.6	134.0 ± 0.4

Ba	709 ± 27	826 ± 65
Cr	198.2 ± 4.7	189.3 ± 4.5
Mn	131.8 ± 1.7	131.8 ± 1.2
Sr	1041 ± 14	1041 ± 79
Th	25.7 ± 1.3	26.9 ± 0.32
U	8.79 ± 0.36	9.18 ± 0.36
V	295.7 ± 3.6	285.7 ± 7.9

From Table 2, in most cases, there is an agreement between the results of this work and the certified values obtained from literature.

Table 3: Results of the elemental abundances of NIST 1633a as a quality control for the epithermal NAA

Element	Certificate/Literature Value	Values obtained in this work
Al	14.3 %	13.8 %
Si	22.8 %	20.2 %

In a bid to ascertain the quality of this work, NIST quality control standard, NIST 1633b and NIST 1633a were subjected to the same experimental procedures of irradiation time, delay and counting time and geometry as the samples of interest for this project work. The elemental concentrations obtained were compared with the certified values as shown in Tables 2 and 3. It can be observed from the tables, that in most cases, there is an agreement between the results of this work and the certified values obtained from literature. Thus the values obtained for the experimental samples can be greatly relied upon and should form a baseline for further work.

3.2 Analytical result

Table 4 show the elements and the concentrations in which they are present in samples collected from the different mining sites in Bagega.

Table 4: Results of the elemental abundances of the experimental samples from Bagega

Element	BW5 (ppm)	BW 6(ppm)	BB 7(ppm)	BS 10(ppm)	Mean(ppm)	Range(ppm)
Mg	BDL	BDL	BDL	BDL	BDL	BDL
Al	20080 ± 401	20270 ± 263	15580 ± 187	17150 ± 274	18270±281	15373-20533
Ca	BDL	BDL	2293 ± 566	BDL	573±566	0-2859
Ti	1206 ± 247	1858 ± 356	BDL	1324 ± 238	1097±210	959-2241
V	137 ± 5	142 ± 6	122 ± 3	118 ± 3	130±4	115-142
Mn	178 ± 1	286 ± 2	122 ± 1	112 ± 1	175±1	111-288
Dy	1.3 ± 0.2	1.0 ± 0.3	1.0 ± 0.2	1.3 ± 0.2	1.15±0.23	0.7-1.5
Na	47 ± 2	33 ± 2	26 ± 1	33 ± 1	35±2	25-49
K	BDL	909 ± 260	460 ± 83	654 ± 111	506±114	377-1169
Br	64.4 ± 0.6	30.6 ± 0.5	38.8 ± 0.5	22.3 ± 0.3	39.03±0.5	22.0-65.0
La	212.0 ± 0.9	97.8 ± 0.6	134.0 ± 0.5	76 ± 1	520±0.8	75-212.9
Sc	3.47 ± 0.08	2.66 ± 0.07	2.28 ± 0.07	3.25 ± 0.07	2.9±0.07	2.73-3.55

Cr	BDL	54 ± 12	BDL	42 ± 11	24±5.8	31-66
Fe	54120 ± 704	51690 ± 672	49530 ± 693	43840 ± 658	49795±682	43182-54824
Sr	3065 ± 3	BDL	BDL	BDL	766±0.8	0-3068
Sb	BDL	2596 ± 3	2676 ± 3	2938 ± 3	2053±2	2593-2941
Cs	3414 ± 204	BDL	BDL	BDL	854±51	0-3618
Ba	BDL	3202 ± 186	4582 ± 174	2740 ± 173	2631±133	2567-4756
Si	224000	395000	394000	465000	369500	224000-465000

The result of the INAA for the four different soil samples from Bagega from Table 4.3, shows that the soil is rich in silicon (Si) (the most abundant) with a mean concentration of 36.98% (369800 ppm) and BW10 having the highest concentration of 46.5% (465000). This is followed by Iron (Fe) with a mean concentration of 49795 ppm and BW5 having the highest concentration of 54120 ppm. Aluminum (Al) has a mean concentration of 18270 ppm and BW6 has the highest concentration of 20270 ppm. Barium (Ba) has a mean concentration of 2631 ppm with BB7 having the highest concentration of 4582 ppm. Antimony (Sb) has a mean concentration of 2053 ppm with BS10 having the highest concentration of 2938 ppm, and titanium (Ti) has a mean concentration of 1097 ppm with BW6 having the highest concentration of 1858 ppm. Thus, the major elements present in Bagega soils follow the trend: Si>Fe>Al>Ba>Sb>Ti. Mg which constitutes major elements in soils was found to be below detection limit in the four samples from Bagega.

Cesium (Cs), Strontium (Sr), Calcium (Ca), Lanthanum (La), Potassium (K), Manganese (Mn) and Vanadium (V) were present in micro concentrations. Cs has a mean concentration of 854 ppm, Sr has a mean concentration of 766 ppm, Ca has a mean concentration of 573 ppm, La has a mean concentration of 520 ppm, K has a mean concentration of 506ppm, Mn has a mean concentration of 175 ppm and V has a mean concentration of 130 ppm..Zinc (Zn) was found to be below detection limit. Sodium (Na), Chromium (Cr) and Bromine (Br) were present in trace concentrations. The sample with code DSR13 which is the uncontaminated soil used in the remediation work at Dareta serves as the control sample for this work. It is observed that there is an agreement between the elemental concentration of the Bagega samples and that of the control in most cases except in V, Sb and Ba where the Bagega soil samples have remarkable higher concentrations.

Table 5: Results of the elemental abundances of the experimental samples from Dareta

Element	DMW1	DR2	DD 3	DS 11	DM 12	DSR 13	DSD 14	DSW 15	Mean	Range
Mg	BDL	BDL	4301 ± 636	1897 ± 574	2875 ± 646	BDL	18510 ± 1073	BDL	3448±366	1323-19583
Al	24970 ± 200	44750 ± 448	73380 ± 660	35060 ± 420	51890 ± 467	70910 ± 567	88630 ± 886	52600 ± 474	55274±515	24770-89516
Ca	BDL	BDL	BDL	BDL	2434 ± 676	3035 ± 746	53710 ± 3276	2692 ± 713	7734±676	1758-56986
Ti	1091 ± 295	2474 ± 341	4069 ± 435	1374 ± 254	4081 ± 375	2600 ± 325	6961 ± 584	2999 ± 333	3206±368	796-7545
V	29 ± 2	55 ± 3	72 ± 4	39 ± 3	151 ± 5	38 ± 3	198 ± 6	51 ± 4	79±4	27-204
Mn	117 ± 1	362.5 ± 1.8	69 ± 2	255 ± 1	362 ± 2	574 ± 2	1415 ± 4	501 ± 2	457±2	67-1419
Dy	1.0 ±0.3	2.8 ± 0.4	5.3 ± 0.4	1.7± 0.3	2.7 ± 0.3	4.5 ± 0.4	4.7 ± 0.6	2.3 ± 0.3	3.13±0.38	0.7-5.7
Na	301 ± 3	518 ± 5	785 ± 3	1561 ± 8	2469 ± 10	9157 ± 18	2294 ± 7	2989 ± 6	2509±8	298-9193
K	13660 ± 246	25300 ± 481	35710 ± 250	11710 ± 468	31420 ± 660	3967 ± 476	BDL	7584 ± 182	16168±345	3491-35960
As	2.8 ± 0.3	3.2 ± 0.2	4.5 ± 0.2	44.6 ± 0.5	52.9 ± 0.4	7.2 ± 0.3	BDL	15.0 ± 0.2	16±0.3	2.8-52.9
Br	BDL	BDL	0.5 ± 0.2	BDL	1.7 ± 0.2	1.5 ± 0.3	BDL	BDL	0.46±0.09	0.3-1.8
La	9.6 ± 0.2	21.8 ± 0.2	31.1 ± 0.2	12.5 ± 0.2	28.5 ± 0.2	18.6 ± 0.3	2.1 ± 0.1	14.6 ± 0.1	17.4±0.19	2.0-31.3
Sm	1.38 ± 0.03	3.63 ± 0.03	6.88 ± 0.03	2.25 ± 0.02	8.70 ± 0.03	4.47 ± 0.03	BDL	3.23 ± 0.03	3.8±0.03	1.35-8.73
Ho	BDL	2.0 ± 0.4	1.8 ± 0.2	1.1 ± 0.2	BDL	0.9 ± 0.2	BDL	BDL	0.73±0.13	0.7-2.4
U	2.2 ± 0.6	5.2 ± 0.5	3.9 ± 0.4	4.9 ± 0.4	3.2 ± 0.4	0.8 ± 0.2	BDL	1.7 ± 0.3	2.74±0.35	0.6-5.7
Sc	3.4 ± 0.7	9.13 ± 0.07	12.77 ± 0.09	4.85 ± 0.05	4.24 ± 0.05	8.6 ± 0.1	26.1 ± 0.1	6.55 ± 0.06	9.46±0.15	2.7-26.2

Cr	20 ± 3	45 ± 3	60 ± 3	30 ± 4	31 ± 3	39 ± 2	317 ± 5	25 ± 2	70.9±3.13	17-322
Fe	27880 ± 335	47680 ± 381	49200 ± 394	35010 ± 315	25690 ± 283	30390 ± 304	68180 ± 545	33610 ± 336	39703±362	25407-68725
Co	2.9 ± 0.3	15.3 ± 0.4	16.2 ± 0.4	5.2 ± 0.3	6.5 ± 0.4	7.7 ± 0.4	41.3 ± 0.7	5.1 ± 0.3	12.53±0.4	2.6-42.0
Zn	BDL	40 ± 37	24 ± 5	36 ± 7	BDL	BDL	BDL	20 ± 6	15±6.9	8.1-77
Rb	53 ± 5	92 ± 6	142 ± 9	45 ± 4	84 ± 6	16 ± 5	BDL	18 ± 3	56.3±4.275	15-151
Sb	BDL	BDL	14.3 ± 0.1	171.5 ± 0.5	122.3 ± 0.5	1.28 ± 0.09	0.7 ± 0.1	34.5 ± 0.2	43±0.19	0.6-172.0
Element	DMW1	DR2	DD 3	DS 11	DM 12	DSR 13	DSD 14	DSW 15	Mean	Range
Cs	35.5 ± 0.3	37 ± 0.2	3.0 ± 0.4	2.1 ± 0.2	2.0 ± 0.3	1.2 ± 0.3	BDL	BDL	10.1±0.2	0.9-35.8
Ba	0.9 ± 0.3	2.1 ± 0.4±	2489 ± 55	1735 ± 57	2050 ± 57	284 ± 35	334 ± 57	1335 ± 38	1028±38	0.6-2544
Nd	112 ± 60	2962 ± 59	BDL	BDL	20 ± 2	19 ± 2	BDL	12 ± 2	391±16	10-3021
Eu	BDL	BDL	1.8 ± 0.2	0.6 ± 0.1	0.5 ± 0.1	BDL	1.6 ± 0.2	1.5 ± 0.2	0.75±0.1	0.4-2.0
Tb	BDL	0.8 ± 0.1	0.5 ± 0.2	0.5 ± 0.1	0.6 ± 0.1	0.8 ± 0.2	0.7 ± 0.2	0.7 ± 0.1	0.58±0.13	0.3-1.0
Tm	0.5 ± 0.1	0.8 ± 0.1	1.0 ± 0.2	BDL	BDL	0.8 ± 0.2	BDL	0.6 ± 0.2	0.46±0.1	0.4-1.2
Yb	BDL	BDL	2.8 ± 0.2	0.6 ± 0.2	0.9 ± 0.2	2.8 ± 0.2	2.03 ± 0.21	2.0 ± 0.2	1.39±0.15	0.4-2.24
Lu	0.6 ± 0.1	2.2 ± 0.2	0.48 ± 0.2	0.26 ± 0.03	0.34 ± 0.03	0.52 ± 0.02	0.32 ± 0.03	0.39 ± 0.02	0.64±0.08	0.23- 2.4
Hf	0.22 ± 0.03	0.42 ± 0.04	12.3 ± 0.3	4.1 ± 0.2	13.3 ± 0.3	6.9 ± 0.2	2.9 ± 0.3	5.5 ± 0.2	5.71±0.2	0.19-12.6
Ta	BDL	2.5 ± 0.2	0.8 ± 0.2	1.1 ± 0.2	BDL	BDL	BDL	BDL	0.55±0.08	0.6-2.7
Th	3.8 ± 0.2	3.3 ± 0.2	6.1 ± 0.2	2.9 ± 0.2	11.3 ± 0.3	5.1 ± 0.2	3.1 ± 0.2	3.8 ± 0.2	4.93±0.21	2.9-11.6
Si	344000	301000	474000	441000	327000	281000	271000	376000	351900	271000-474000

All results are in ppm; BDL = Below Detection Limit

From Table 5, the most abundant element in Dareta mining site is Si with a mean concentration of 35.19% (351900 ppm) and DD3 having the highest concentration of 47.4%. This is followed by Al with a mean concentration of 55274 ppm, with DD3 having the highest concentration of 73380 ppm. Fe has a mean concentration of 39703 ppm and a maximum concentration of 68180 ppm from DSD14. K has a mean concentration of 16168 ppm and a maximum concentration of 35710 from DD3. Ca has a mean concentration of 7734 ppm and a maximum concentration of 53710 from DSD14. Mg has a mean concentration of 3448 ppm and a maximum concentration of 88630 ppm from DSD14. Ti has a mean concentration of 3206 ppm and a maximum concentration of 6961 ppm from DSD14. Na has a mean concentration of 2509 ppm and a maximum concentration of 9157 from DSR13 and Ba has a mean concentration of 1028 ppm and a maximum

concentration of 2489 ppm from DD3. Thus, the trend of the elemental distribution tend to follow the order : Si>Al>Fe>K>Ca>Mg>Ti>Na>Ba. Present in minor concentrations are Mn with a mean concentration of 457 ppm and Nd with a mean concentration of 391 ppm. As which has an outstanding presence in many soil analysis from mining has a trace concentration of 16 ppm. Comparatively, the samples from the other Dareta soil samples had an agreement in terms of elemental concentration with the control except in the element Ba where the samples have outstanding higher concentrations and in Mg where the control's concentration was found to be below detection limit

Table 6shows the result of the elemental composition and concentration of the experimental soil samples obtained from the Sunke mines.

Table 6: Results of the elemental abundances of the experimental samples from Sunke

Element	SM 4	SF 8	SF 9	Mean	Range
Mg	3502 ± 819	3807 ± 822	BDL	2436±547	2683-4629
Al	71640 ± 644	95160 ± 1141	110300 ± 1103	92367±963	70996-111403
Ca	5442 ± 1001	3919 ± 932	3830 ± 923	4397±952	2970-6443
Ti	3942 ± 346	4811 ± 442	4272 ± 482	4342±423	3596-5253
V	111 ± 5	105 ± 5	70 ± 5	95±5	65-116

Mn	346 ± 2	314 ± 2	317 ± 2	326±2	312-346
Dy	3.8 ± 0.3	5.4 ± 0.3	5.8 ± 0.3	5±0.3	3.5-6.1
Na	1906 ± 6	2481 ± 5	1852 ± 4	2080±5	1848-2486
K	19670 ± 236	17090 ± 239	21170 ± 234	19310±236	16851-21404
As	51 ± 0.3	47.3 ± 0.3	14.6 ± 0.2	38±0.3	14.4-51.3
Br	1.6 ± 0.2	1.9 ± 0.2	2.1 ± 0.2	1.87±0.2	1.4-2.3
La	32.0 ± 0.2	27.6 ± 0.2	35.8 ± 0.2	31.8±0.2	27.4-36.0
Sm	6.06 ± 0.03	5.22 ± 0.03	6.32 ± 0.03	5.87±0.03	5.19-6.35
Ho	BDL	1.5 ± 0.2	0.9 ± 0.2	0.8±0.13	0-1.7
U	2.0 ± 0.2	2.9 ± 0.4	2.3 ± 0.3	2.4±0.3	1.8-3.3
Sc	10.94 ± 0.08	BDL	9.59 ± 0.07	6.84±0.05	0-11.02
Cr	47 ± 4	23 ± 4	43 ± 3	37.67±3.67	19-51
Fe	25960 ± 312	22480 ± 337	23070 ± 254	23837±301	22143±26272
Co	7.6 ± 0.3	2.3 ± 0.3	6.7 ± 0.3	5.53±0.3	2.0-7.9
Zn	452 ± 13	BDL	770 ± 13	407±9	0-783
Rb	70 ± 6	203 ± 7	71 ± 5	115±6	64-210
Sb	146.5 ± 0.4	BDL	BDL	49±0.13	0-146.9
Cs	4 ± 1	BDL	4.2 ± 0.3	2.7±0.43	0-4.5
Ba	620 ± 41	BDL	661 ± 38	427±26	0-699
Nd	18 ± 3	19 ± 3	23 ± 2	20±2.67	15-25
Eu	1.2 ± 0.2	BDL	1.2 ± 0.1	0.8±0.1	0-1.3
Tb	0.8 ± 0.2	1.60 ± 0.09	0.8 ± 0.1	1.07±0.13	0.6-1.69
Tm	BDL	1.8 ± 0.3	1.0 ± 0.2	0.93±0.167	0-2.1
Yb	2.4 ± 0.3	BDL	3.0 ± 0.2	1.8±0.167	0-3.2
Lu	0.50 ± 0.03	BDL	0.56 ± 0.03	0.35±0.02	0-0.59
Hf	7.9 ± 0.3	2.2 ± 0.2	7.6 ± 0.2	5.9±0.23	2.0-8.2
Ta	BDL	BDL	0.9 ± 0.1	0.9±0.2	0-1.0
Th	8.1 ± 0.3	1.7 ± 0.2	7.0 ± 0.2	5.6±0.23	1.9-8.4
Si	30500	665000	356000	442000	305000-665000

All results are in ppm; BDL = Below Detection Limit

From Table 6, the most abundant element in Sunke mining site is Si with a mean concentration of 44.2% (442000 ppm) and SF8 having the highest concentration of 66.5%. This is followed by Al with a mean concentration of 92367 ppm and a maximum concentration of 110300 ppm from SF9. Fe has a mean concentration of 23837 ppm and a maximum concentration of 25960 ppm from SM4. K has a mean concentration of 19310 ppm and a maximum concentration of 21170 ppm from SF9. Ca has a mean concentration of 4397 ppm and a maximum concentration of 5442 ppm from SM4. Ti has a mean concentration of 4342 ppm and a maximum concentration of 4811 ppm from SF8. Mg has a mean concentration of 2436 ppm and a maximum concentration of 3807 ppm from SF8. Na has a mean concentration of 2080 ppm and a maximum concentration of 2481 ppm from SF8. Present in minor concentrations are Ba with a mean concentration of 427 ppm, Zn with a mean concentration of 407 ppm, Mn with a mean concentration of 326 ppm and Rb with a mean concentration of 115 ppm. As which has an outstanding presence in many soil analysis from mining has a trace concentration of 38 ppm. Thus the trend followed by the elements with major concentration Sunke soil is: Si>Al>Fe>K>Ca>Ti>Mg>Na. There is an agreement between the Sunke elemental concentration and that of the control, except that the Mg present in the sample was below detection limit.

Making a comparison between the major elements found in the samples from the three study areas, it is found that Si determined from Sunke mine samples has the highest concentration. The second most abundant element is Al with Sunke samples also having the highest concentration. Si, Fe and Al were detected to be in appreciable concentrations in the three study areas.

3.3 Comparison between the level of Trace Elements present in the experimental samples and the Maximum Allowable Concentrations (MAC) in various countries.

Trace elements occur naturally in soils and are needed as essential nutrients in small quantities. However at elevated levels, all trace elements become potentially toxic (Hooda, 2010). Different countries set different concentrations as permissible concentrations to be found in soils. Table 7 shows the MAC of trace elements in soils for different countries.

Table 7: Maximum Allowable Concentrations(MAC) of Trace Elements in Agricultural Soils Proposed in the Directives in Various Countries and Different Years (ppm DW) (Kabata-Pedias and Pedias, 2001).

Element	Austria 1977	Poland 1977, 93	Germany 1984	Russia 1986	UK 1987	US 1988	Germany 1992	Euro Comm. 1986	US 1993
As	50	30	20	2	10	14	-	-	-
B	100	-	25	-	-	-	-	-	-
Be	10	10	-	-	-	-	-	-	-
Cd	5	1-3	3	-	3-15	1.6	1.5	1-3	2050
Co	50	50	-	-	-	20	-	-	-
Cr	100	50-80	100	0.06	-	120	100	30-150	1500
Cu	100	30-70	100	23	50	100	60	50-140	750
F	500	-	200	-	-	-	-	-	-
Hg	5	5	2	2.1	-	0.5	1	1-1.5	8
Mo	10	10	-	-	-	4	-	-	-
Ni	100	30-75	50	35	20	32	50	30-75	210
Pb	100	70-150	100	20	500-2000	60	100	50-300	150
Se	10	10	10	-	-	1.6	-	-	-
V	-	150	-	150	-	-	-	-	-
Zn	300	100-300	300	110	130	220	200	150-300	1400

Table 8 shows the concentration of trace elements in the experimental samples collected from the different mine sites.

Table 8: Concentration of Trace Elements in the experimental samples (ppm)

Element	DMW1	DR2	DD3	SM4	BW5	BW6	BB7	SF8	SF9	BS10	DS11	DM12	DSR13	DSD14	DSW 15
As	2.8	3.2	4.5	51	-	-	-	47.3	14.6	-	44.6	52.9	7.2	BDL	15
Co	2.9	15.5	16.2	7.6	-	-	-	2.3	6.7	-	5.2	6.5	7.7	41.3	5.1
Cr	20	45	60	47	BDL	54	BDL	23	43	42	30	31	39	317	25
V	29	55	72	111	137	142	122	105	70	118	39	151	38	198	51
Zn	BDL	40	24	452	-	-	-	BDL	770	-	36	BDL	BDL	BDL	20

BDL= Below Detection Limit.

Table 8 shows the analyzed trace elements present in the experimental samples and the concentrations in which they are present. Making a comparison between these values and the Maximum Allowable Concentration of trace elements in different countries as presented in Table 4.6, it is observed that the concentration of almost all trace elements present in the experimental samples are still within the allowable concentration of some countries. Thus, the presence of trace elements have been established, though not in concentrations to pose health hazards. Care must be taken so that the allowable concentrations are not exceeded however as some of the concentration of these trace elements in the samples are slightly above the allowable concentration. An instance is the concentration of V measured in DSD13 which is 198 ppm as against the MAC of 150ppm. There is also the case of As where SM4 had 51 ppm and DM12 52.9 ppm as against the MAC of 50 ppm. Though these are slight differences, caution should be exercised.

IV. CONCLUSION

Thermal and Epithermal Neutron activation analysis has been carried out on 15 different samples collected from three different areas in Anka LGA namely Bagega, Dareta and Sunke. From the activation analysis, 34 elements were successfully determined with just about ten having up to 0.1% concentration (1000 ppm) in the samples. A comparison was made between the concentration of trace elements measured in the samples and the Maximum Allowable Concentration (MAC) of various countries. Most of the trace elements were present in concentration within the MAC except for a few elements that had concentrations slightly above the MAC. Although values of these metals are within acceptable range of some countries, there is an indication of some heavy metal pollution in the mining areas. This has potential health implications and could result in endemic diseases.

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