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Elemental Analysis of Soil Around Ikot Abasi Aluminum Smelter Plant, Nigeria By Instrumental Neutron Activation Analysis (INAA)

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ABSTRACT

Concentration of major, minor and trace elements in soil samples around Ikot Abasi Aluminum Smelter Company of Nigeria (ALSCON) Ikot Abasi, Nigeria were determined by Instrumental Neutron Activation Analysis (INAA) technique using thermal neutron from Nigeria Nuclear Research Reactor (NIRR-1) at Center for Energy Research and Training (CERT), Ahmadu Bello University Zaria. By this analysis, 25 elements were determined in the soil around Ikot Abasi Aluminum Smelter Plant the element include Cr, Yb, Cs, Sb, Fe, Sm, Dy, Pa, As etc. The results show that INAA of soil samples around the studied area gave maximum values of 9.99 ± 0.41 ppm for As; 9.54 ± 1.06ppm for Sb; 7.725 ± 1.53ppm for Lu; 4.28 ± 0.81ppm for Fe and 3.24 ± 0.18ppm for Cr.

Key word: Soil, Neutron, Activation Analysis, Aluminum Smelter Plant, Ikot Abasi.

INTRODUCTION

The State of the contamination of our environment has an overwhelming effect on the quality of human health. The abatement of pollution arising from various human activities has been a subject of great concern for institutions and governments worldwide. Human activities essentially lead to elevated level of air, soil, and water pollution. Air pollution and water pollution can have inimical effect to soil thereby altering its elemental composition. Thus soil is the mother of the universe, and must be given a first treatment. Elemental analysis of soil particles has become important, because of the effects of these particles on the environment and health [1]. It has also been observed that elemental association with natural sources, such as soil and ocean are usually found with the coarse particulate, while elements emitted from anthropogenic sources are associated with the fine particulate [2]. Anthropogenic sources have also be found to be responsible for the concentration of trace metals in tree barks [3].

Damage, done to body organs and tissues affect human health as a result of absorption and contaminated particles, which contain heavy metals and trace elements. Asthma cough, anemia, loss of vision, renal failure and infertility may be the associated health problems [4, 5, 6]. Sources of particles that accounted for 82% of the total measured particles have been identified to include: motor vehicle (45.4%), secondary particles (16.6%), road dust (12.7%) and di-icing salt (7.5%) [7]. Similarly, it has also been reported that soil was identified as accounting for majority of contaminated particles [8]. Target transformation recap model has been employed to determine boston urban aerosol, they study identified soil sources namely, soil, residual fuel oil burning refuse incineration, marine, motor vehicle exhaust and road dust [9]. There have been several studies of contribution of automobile transport to levels of urban air pollution in Nigeria. Concentrations of CO and Co_2 in some locations in Ibadan and its rural suburbs has been determined [10].

Lead pollution of motor vehicles is capable of causing serious health consequences such as impairment of circulatory, reproductive and nervous systems as well as kidney problems. Lead has also been linked with hyperactivity and lowered learning ability in children. Apart from lead, Pb emission, other elements, which are constituents of crude oil such as V, Cd and As are released into the atmosphere during combustion of petroleum products. Others like Fe, Ni, Cr, Sb, Zn, which are essential components of motor vehicle parts such as tyres and brake, are also emitted as a result of wear and tear. Some of these elements when the concentration is above limits of being essential in the body can be very toxic by causing numerous health hazards. The exposure of human beings, plants and animals to toxic trace pollutants in the ambient outdoor air depends primarily on the amount emitted; proximity to sources and prevailing weather conditions, these toxic elements could have a reasonable high resident time in the ambient air and eventually settle down on soils' surface. Constituents of crude oil such as V, Cd and As are released into the atmosphere during combustion of Petroleum products. There is no doubt that air pollution and soil pollution constitute major health hazard to environmental subsystems. Pollution is generally a by-product of industrialization; therefore one is faced with the problem of improving air and soil qualities and retaining the industrialization of the nation [11].

For this analysis, soil samples around Ikot Abasi Aluminum Smelter plant was analyzed for elemental content by Nuclear Activation Analysis (NAA) using thermal neutrons from the Nigerian Research Reactors (NIRR-1). INAA for time and season has become a powerful instrument for many authors for the analysis of various samples of interest. Elemental content of rock samples from Ugep Area of Cross River State Nigeria using the Instrumental Neutron Activation Analysis [12]. The INAA has been used, to determine large data sets of elements in Nigerian Coal subject to cluster procedures [13]. The INAA technique has been used to evaluate the homogeneity of reference samples of soil [14]. Ceramic wares used in our homes have been found to contain high levels of heavy metals in varying concentrations [15].

NAA is an irradiative process that take place in the nuclei of elements. The physical phenomena upon which NAA are based on the properties of nucleus, radioactivity and the interaction of radiation with mater. About 70% of the elements have nuclide possessing properties suitable for NAA [15]. Instrumental Neutron Activation Analysis (INAA) is the application of purely instrumental procedures for elemental analysis that is the use of automated sample handling gamma-ray spectroscopy with solid-state detectors and computerized data processing. With this method, it is possible to measure more than thirty elements in a sample various applications of INAA ranging from the analysis of biological materials to ambient air particulate matter has been reported in numerous journal articles [17, 18, 19].

Elemental analysis of the total suspended matter of down town Caracas was conducted with a combination of XRF and NAA are reported [20]. They found out that soil is the best absorber of elemental particulate. Harmattan dust collected with Anderson H-volume sampler with cascade impactor has been analysed and also measured the concentrations of 28 elements [21].

There are limited data available of the elemental composition of soil particles in Ikot Abasi Local Government Area which is the industrial site of Akwa Ibom State, and has led to the conclusion that many elements are present in higher concentrations than could be expected. It therefore becomes imperative to determine the elemental concentration in soils around Ikot Abasi Aluminum Smelter plant by INAA.

MATERIALS AND METHODS

The Aluminum Smelter Company of Nigeria Limited (ALSCON) is sited at Ikot Abasi, the industrial area of Akwa Ibom State. It uses an independent gas turbine to generate electricity needed to run the plant. The power plants generate a total capacity of 540mw of electricity. Soil samples were collected around Ikot Abasi Aluminum Smelter plant at ten locations (Table 1).

Table 1: Soil sampling sites and their distances from Ikot Abasi Aluminum Smelter Plant, Nigeria (ALSCON)

Site Code	Sampling Site/Code
KTSO1	Located at Sir Udoma round about, approximately 4km north-west of the Plant. Closed to the central motor park.
KTSO2	Located along ALSCON access road, approximately 0.5km north-east of the plant, within the influence of the aluminum smelter plant, and the propose Akwa Ibom refinery.
KTSO3	Located at Uta Ewa beach, approximately 6km south-east of the plant. This is fishing settlement. Out board engine boats were visible at the beach used for fishing and transportation within the water ways.
KTSO4	Located at the Ikot Abasi central market, approximately 5km north of the aluminum smelter plant. It is a daily and big market, that services the city dwellers.
KTSO5	Located near the Berger Jetty approximately 0.4km south of the plant. Ship and speed engine boats were visible at the Jetty during the three weeks sampling.
ETEO1	Location at Ete Town, approximately 10km father north in the east direct. This is a big daily market that services. Most of the villages and towns in nearby Local Government Area.
SENO1	Located at Essene Town of Ikpa Ibom, approximately 16km of the Ikot Abasi aluminum smelter plant.
AYAO1	Located at Atan Ikpe Town of Edem Aya, approximately 18km furthest north of the Ikot Abasi aluminum smelter plant.
KWAO1	Located at Okon Town approximately 11km from the plant, and within the residential area. The site is close to the Methodist Church Nigeria, Ikwa town.
KONO1	Located at Okon Town approximately 14km farther north in the east direction. This site is within small scale industrial area close to auto mechanic workshop where motor parts are fabricated.

The soil samples were collected around the Smelter plant at sites which are between 0.4km and 18.0km range from the plant (Table 1).

The top surfaces of the soils at the ten sites were scraped off to a depth of 20cm. This was to remove any trace of contamination of top soil surface within the first 20cm depth, as a result of human activities. Thereafter, 5kg weight of field samples of the soil at each of the sites were collected, thoroughly mixed and sieved, loaded in a labeled polythene bags and transported to the laboratory for analysis.

The soil samples collected from the field were quartered and exposed to ambient air in a dust free environment. Thereafter, the samples were dried to a constant for 48 hours in a monitored KETONG 101 oven maintained 50^{o}C in the balance from at Center for Energy Research and Training (CERT). The dried samples were re-homogenized and quartered. 150mg of each soil samples was weighed and wrapped in polyethylene film and heat sealed. Two samples were prepared from each location for long and short irradiation respectively.

For elements leading to long lived activation products, samples were picked and heat-sealed in one 7cm^3 rabbit capsules. The capsule takes as much as 20 samples, the neutron flux variation along the capsule is less than three percent.

The polyethylene bags were prepared in the balance room in order to avoid contamination and maintain high quality. The polyethylene sheet was cut with a pair of scissors and sealed into a rectangular bag of approximately 2cm by 5cm dimension using impulse sealer ME-200H. The bags were soaked in diluted nitric acid for 24 hours and then put in distilled water and rinsed twice before they were dried in an over for 24 hours at temperature of 60^{o}C. It was after the polyethylene bags were treated in this way that they were used to package the samples for irradiation and counting.

Samples were pulverized and 150mg sub-samples were weighed and wrapped in polyethylene films for irradiation. Samples were prepared for two regimes of irradiation (short and long irradiation) depending on activation products.

For short irradiation the samples were each packed in 7cm^3 rabbit capsules and irradiate in turn in an outer irradiation channel B4, where the neutron spectrum is “soft”. For elements leading to medium lived and long-lived activation products, the samples were packed in 7cm^3 rabbit capsules for irradiation. Each capsule was irradiated for 6hrs in the small outer irradiation channels (A1, B2 and B3) where the thermal neutron is maximum.

The first round of counting was for 10 minutes, following the short irradiation (SI), which is performed after a waiting time 2-12 minutes. Samples were counted using a plexi-glass holder designated as “V5” which corresponds to a source-detector geometry of 15cm. The second round of counting also for 10 minutes, following the short irradiation (S2), was performed after a waiting period of 3-4 hours. Samples were counted using a plex-glass holder designated as “V1” corresponding to a source-detector geometry of 1.8cm. For the long irradiation, the first round of counting was for 30 minutes, following the long irradiation (L.1), which was performed after a waiting period 2-3 days. Samples were counted using a plex-glass holder designated as “V1” corresponding to a source-detector geometry of 1.8cm. The second round of counting was for 60 minutes following the long irradiation (L.2), which was performed after a cooling time of 10.15 days. Samples were counted using a plex-glass holder designated as “V1” corresponding to a source-detector geometry of 1.8cm.

The choice of cooling time was such that detector’s dead time was controlled to be less than 10%. Two certified reference materials, IAEA-soil 7 and GSD-5 were used as a analytical quality control material to validate the procedure for all the element.

RESULTS AND DISCUSSION

Table 2 gives the results of the concentrations for the elements detected in the soil around the Ikot Abasi Aluminum Smelter Plant by the Instrumental Neutron Activation Analysis Technique (INAA). Some of the elements are represented in Table 2 as "BDL" because they are below the detection limit of the instrument but may be above zero [22]. As shown in the table, it was possible with the instrumental neutron activation analysis technique to determine up to twenty five elements in the soil samples.

Table 2: Elemental concentrations in soil around Ikot Abasi Aluminum Smelter Plant by INAA with NIRR-1 (values in ppm)

Equipment	SOKTSO1	SOKTSO2	SOKTSO3	SOKTSO4	SOKTSO5	SOETE01	SOSEN01	SOAYA01	SOKWA01	SOKON01
Na	4.24±0.05	5.63±0.03	2.68±0.04	7.01±0.09	7.60±0.05	3.92±0.07	3.93±0.08	2.38±0.06	2.59±0.07	3.51±0.08
Mg	BDL	BDL	BDL	BDL	2.95±0.31	BDL	BDL	BDL	BDL	BDL
Al	3.37±0.01	1.94±0.01	1.53±0.01	3.82±0.01	3.36±0.01	1.17±0.01	2.38±0.01	2.91±0.01	2.15±0.01	3.45±0.01
Ca	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND	ND
Ti	4.23±0.07	1.47±0.13	2.70±0.07	2.83±0.09	2.56±0.09	1.96±0.10	3.01±0.08	3.82±0.07	3.06±0.08	4.49±0.07
V	3.75±0.07	1.87±0.09	2.35±0.07	3.78±0.07	3.58±0.07	1.42±0.10	2.41±0.07	3.33±0.07	3.06±0.07	4.89±0.06
K	2.67±0.18	1.72±0.05	2.30±0.18	1.467±0.07	1.87±0.09	2.47±0.34	2.15±0.33	1.84±0.35	2.55±0.42	2.90±0.47
Mn	7.42±0.04	9.05±0.12	9.21±0.12	5.66±0.10	6.78±0.11	1.24±0.01	5,23±0.01	5.25±0.11	0.81±0.09	2.91±0.02
Dy	3.09±0.16	6.24±0.34	2.86±0.24	1.22±0.24	2.77±0.17	1.40±0.17	1.04±0.23	2.13±0.11	1.39±0.17	1.87±0.16
Ga	3.34±0.19	1.48±0.26	1.08±0.10	4.37±0.38	3.10±0.46	1.92±0.27	2.86±0.33	3.95.036	2.94±0.33	3.05±0.37
As	7.31±0.26	7.45±0.34	7.37±0.24	1.74±0.05	1.26±0.05	6.56±0.034	6.43±0.33	9.99±0.41	7.47±0.38	8.87±0.40
Br	1.95±0.04	5.85±0.35	8.05±0.26	2.29±0.05	1.03±0.05	1.17±0.04	1.45±0.04	1.54±0.04	1.07±0.04	1.40±0.05
Sb	9.54±1.06	3.14±0.17	8.589±0.89	7.46±1.04	BDL	1.29±0.09	9.42±12.07	6.56±0.88	6.39±0.97	1.02±0.17
La	7.06±0.04	2.83±0.03	4.58±0.03	3.48±0.04	4.73±0.04	4.20±0.04	4.83±0.04	4.98±0.04	6.73±0.05	5.79±0.05
Sm	2.35±0.10	1.14±0.04	1.62±0.07	1.34±0.06	1.81±0.08	1.77±0.08	1.23±0.06	1.39±0.06	2.17±0.10	1.90±0.08
Cr	ND	ND	2.01±0.15	1.56±0.17	3.16±0.20	3.24±0.18	ND	ND	BD2	
Fe	1.282±0.13	4.282±0.81	2.130±1.14	ND	ND	ND	ND	1.227±0.72	BD_2	BD_2
Ba	3.01±0.17	1.32±0.10	5.23±0.23	2.75±0.15	2.85±0.15	3.23±0.16	2.44±0.15	ND	BD_2	BD_2
Yb	ND	ND	3.41±0.31	ND	ND	ND	ND	ND	BD_2	BD_2
Lu	7.72±1.53	NP	4.30±1.24	2.94±1.38	ND	ND	ND	1.52±0.22	BD_2	BD_2
Hf	ND	ND	BDL	BDL	5.37±.177	ND	ND	ND	BD_2	BD_2
Ta	1.54±1.05	ND	1.02±0.65	BDL	ND	ND	4.99±1.86	ND	BD_2	BD_2
Pa	ND	ND	BDL	BDL	ND	ND	ND	ND	BD_2	BD_2
Cs	ND	ND	ND	ND	ND	ND	ND	1.25±0.14	BD_2	BD_2
Ce	ND	ND	ND	ND	ND	ND	ND	2.63±0.25	BD_2	BD_2

(1) BDL = Below Detection Limit
(2) ND = Not Detected
(3) BD_2 = 2^{nd} counting was not possible due to equipment breakdown.

The heavy metals detected were Cr, Yb, Cs, Sb, Lu, Fe, Sm, Dy, Pa and As, among others. Arsenic, which is a semi-metallic element, is known to be strongly poisonous, while protactinium is a radioactive metallic element. These elements presence in the soil poses a serous threat to human health, especially when they find themselves into edible crops, through their roots. Magnesium and calcium are scarcely present in the trace element category in the soil samples around the ALSCON Plant. The degradation of organic substances for pollutants largely depends on the microbial species in the soil which is a function of the organic fraction of the soil [23].

A number of pollutants known to degraded in soil and water ranges from industrial waste, municipal waste, to pesticides and to petroleum hydrocarbon [24]. Natural biodegradation in soil

is a slow process and has been attributed to microbial species and their synergistic interaction which determines the fertility or the nutrients status of the soil [25].

Arsenic is a widely distributed metalloid, occurring in rock, soil, water and air. Inorganic, arsenic is present in groundwater used for drinking in several countries all over the world (e.g. Bangladesh, Chile and China), whereas, organic arsenic compounds (such as arsenobetaine) are primarily found in fish, which thus may be taken by human [26].

Smelting of non-ferrous metals and the production of energy from fossil fuel are two major industrial processes that lead to arsenic contamination of air, water and soil, smelting activities being the largest single anthropogenic source of atmospheric pollution [27].

Two soil samples, SOKWA01 results are not complete, as seen in the table, this was due to the breakdown of the detector facility. The break down of this facility made it impossible for the second counting to take place for these two soil samples. The second counting for these soil samples, would have accounted for the status of elemental concentration of the last ten elements on the above table for the two soil samples.

Table 3: Result of Elemental content of certified standard material IAEA – soil 7 using NIRR-1

Element	Nuclide	Gamma Energy (E_y) KeV	Confidence Value (ppm)	Range (ppm)	This work (ppm)
Na “	^{4}Na “	1368.5 2754.0	- -	- -	16660±67 16770±218
K	^{42}K	1524.6	24900	17700-32100	24830±397
Ga	^{72}Ga	834.1	-	-	16.33±2.10
As	^{76}As	559.1	23.6	22.9-24.3	21.18±0.59
Sb	^{122}Sb	564.2	1.81	1.62-2.60	2.16±0.37
La “	^{140}La “	487.0 1596.2	40.4 40.4	33.1-47.7 33.1-47.7	30.94±1.27 37.35±0.97
Dr	^{32}Br	776.5	85	60-110	64.81±2.92
Sc	^{46}Sc	889.3	13.52	11.53-15.51	13.14±0.11
Cr	^{51}Cr	320.1	84	80.88	77.73±3.73
Fe “	^{50}Fe “	1099.3 1291.6	37400 37400	36700-38100 36700-38100	36680±550 34400±585
Co “	$^{6=}$Co “	1173.2 1332.5	13.7 13.7	13.0-14.4 13.0-14.4	14.17±0.57 13.61±0.35
Cs “	^{134}Cs “	795.8	12.5 12.5	10.4-14.6 10.4-14.6	11.30±0.35 12.64±0.55
Ba “	^{131}Ba “	123.8 496.3	- -	- -	319.6±21.4 509.3±61.6
Ce	^{141}Ce	145.4	-	-	84.98±3.82
Sm	^{153}Sm	103.2	6.86	6.50-7.22	7.37±0.35
Eu “	^{152}Eu “	964.2 1408.0	1.25 1.25	0.89-1.61 0.89-1.61	1.41±0.11 1.31±0.15
Yb “	^{175}Yb “	282.5 396.3	3.04 3.04	2.19-3.89 2.19-3.89	1.89±0.56 3.24±0.26
Th	^{233}Pa	312.0	14.3	12.2-16.4	14.96±0.42

Two reference materials IAEA soil 7 and GSD 5 were used as analytical quality control to validate the procedure for all the elements in the soil samples. The concentration of each of the elements determined from this work was compared with certified values shown on Tables 3. The

results show that the concentrations are better than 5% for most of the elements. The quality control for the experiment have justified the accuracy of the results since most of the elements determined are in good agreement with the certified values except in few cases.

CONCLUSION

The INAA technique has lead to a successful determination of twenty five elements in the soil around the research area. The elements determined include heavy metals like Cr, Yb, Cs, Sb, Lu, Fe, Sm, Dy, Pa and As among others. Some of these heavy metals have been known to be toxic and dangerous to human health especially when found in ground water and growing crops. Some values of their concentration were as high as 9.99 ± 0.41ppm for As, 9.54± 1.06ppm for Sb, 7.72 ± 1.53ppm for Lu, 4.28 ± 0.81ppm Fe, and 3.2 ± 0.18ppm of Cr.

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