



Instrumental Neutron Activation Analysis of Aerosol Particles in Lapai Metropolis

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$$\min \sum_{i=1}^n w_i x_i$$

$$s.t. A_{(n+w) \times n} X_{n \times 1} \geq b_{(n+w) \times 1}$$

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ABSTRACT

A systematic study has been developed to check the quality of air in Lapai metropolis, Niger State, Nigeria. Aerosol samples were collected from four strategic locations during the period of June 2011, using the Gent Stacked sampler in order to characterize the elemental abundances in fine dust particles. In the application of Neutron Activation Analysis technique, the concentration of some heavy trace elements in the atmospheric aerosol were determined in which Vanadium and Manganese have been observed to be relatively lower compare to other elements. The computer software WINSPAN-2004 was used for peak identification, spectra evaluation and determination of the elemental concentrations of Calcium, Magnesium, Aluminum, Titanium and Sodium which revealed possible anthropogenic inputs into the air by means of automobile exhaust emissions, bush burning, welding activities and wind directional movement.

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Introduction

Air pollution is a serious problem in many parts of the world especially in developing countries. Air pollutants are being emitted from natural and anthropogenic sources which give the global world an overall concern as it affect the climatic effect of greenhouse gases which tend to overlap the atmosphere pollution [12]. There are literally thousands of pollutants present in the atmosphere and are trace contaminants either by themselves or upon interaction with other pollutants, there by having adversely impact on our environment [1] [11] [3]. Airborne particulate matter (APM) is more directly affecting human, leading to the need for strict governmental regulations on air pollutants. These air pollutants do not remain confined near the source of emission, but spread over distances, transcending and meteorological condition especially wind direction and speed based on the vertical and horizontal thermal gradient [4].

The overall negative impact on the environment as a result of indoor radon, urban smog, regional acid deposition, destruction of stratospheric ozone and rapid global warming are undesirable. Fine dust and fly ash emitted in the atmosphere or in workrooms can have long residence times in the air thereby becoming potential hazards for human health and the environment. Ash slag and sludge are disposed as landfill materials which give rise to contamination by various substances such as heavy metals.

Aerosol particulates in the atmosphere have direct and indirect effects on the Earth's climate. The direct effect is related to their optical properties. They scatter and/or absorb solar and terrestrial radiation. The level of scattering and absorption depends on their physical and chemical characteristics. Consequently, aerosol act to modify the Earth's radiation budget and thus influence the warming/cooling of the planet.

Aerosol particulates can also act to modify the properties of clouds (indirect effect). Some aerosols in the ambient air act as cloud condensation nuclei (CCN). The formation of cloud droplets is thus promoted by the presence of these particles. The main results are clouds forming at the lower level of super saturation where there are aerosols. Homogeneous nucleation of water droplets occur only at very high levels of super saturations, which are not observed in the Earth's atmosphere [5]. Consequently, heterogeneous nucleation (water drops nucleating on aerosols) is the main mechanism for the formation of clouds, so as fog. The nucleation and growth rates of the cloud droplets depend on the physico-chemical properties of aerosols [2]. Here we focus on aerosols that are usually associated with fogs. In the troposphere, a significant portion of aerosols is anthropogenic in origin. Since fogs are close to the surface, they are affected by aerosol that is in the lower atmosphere, usually close to their source of emission.

As a result of the particulates/pollutants such as Cr, Fe, Mn, Ti, and V found in dust particles, we need an accurate knowledge of the nature and their concentrations as well as their major sources and their pathways through the environment. Thus, the emissions from different sources such as car exhausts, welding activities, carpentering activities, exhausts of large and small size generators, large building constructions, large scare farming activities within Lapai metropolis which combined to form polluted air have been analyzed using instrumental neutron activation analysis (INAA) in order to characterize the elemental abundances.

The accurate determination of trace concentrations of elements in complex matrices (fine dust particles) is very important. Methods that can be used for the analysis of fine dust particles include; atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) or mass spectrometry (MS), all of which require

dissolution and sometimes subsequent chemical treatment of the sample to ensure full dissolution with the inherent risk of contamination.

However, Instrumental Neutron Activation Analysis (INAA) with widest acceptance and unique advantages such as sensitivity, precision, low matrix effects, and preservation of sample has been used extensively to determine the concentration of elements in some varieties of matrices.

Instrumental Neutron Activation Analysis (INAA), as an analytical technique, involved the use of neutrons sourced from nuclear reactors [13]. The exploitation of INAA technique began in the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, using the Miniature Neutron Source Reactor (MNSR), code-named Nigeria Nuclear Reactor-1 (NIRR-1), the 14-MeV Neutron Generator and a 5 Ci $^{241}\text{Am}/\text{Be}$ source with the analysis of trace elements in geological samples, specifically relating to soil fertility and solid mineral studies.

Experimental Procedure

Fine dust particles (polluted air) were collected at different locations in Lapai town and at the outskirts of the town due to serious anthropogenic activities going on in this part of Lapai local government of Niger State, Nigeria. The samplings were carried out during the busy days between the hours of 10:00 am – 4:00 pm. The dust particles were collected using Gent stacked air sampler equipped with stacked filter unit (SFU) for PM10 and PM 2.5 monitoring. The Gent sampler carries two 47 mm diameter nucleopore polycarbonate filters of 8.0 μm to 0.4 μm pores sizes that were used in the first and second stages respectively. The sampler inlet is a PM 10 separator enabling collection of only coarse particles (PM 10 – PM 2.5) having diameters between 2.5 μm and 10 μm while the fine filter collects the size fraction < 2 μm AD. The air particulates were sampled at a slow flow rate of 17 L/min [14] which allowed the collection of PM 2.5 in the second stage. The sampler inlet is a PM 10 separator enabling collection of only coarse particles (PM 10 – PM 2.5) having aerodynamic diameter between 2.5 μm and 10 μm . The filter papers were replaced daily by new ones to collect new samples at each site. The particles actually settle on the surface of the filter paper and the field-blanks were taken on daily basis at each site. The filters were suspended at a height of 2 m above the vacuum pump during sampling to minimize copper contamination from pump motors. The samples were collected during the pre-rainy season period (dry season) between 20th and 25th, June 2011. Elemental analyses were performed by Instrumental Neutron Activation Analysis (INAA) in Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria where the Miniature Nuclear Reactor is situated. The filter loads (sample weight) were measured by means of gravimetry using a balance with 0.1 μg sensitivity. The descriptions of the samples for each site are shown in the Table 1.

Table 1: Description of the air particulates samples for each site

Sample Identity	Sample Weight (g)	Sample Time (hrs)	Sample Site
A 421	0.299	2.500	Outskirt of Lapai
A 423	0.237	2.000	Inside Lapai (T-Junction)
A 425	0.268	3.500	Senate Building
A 427	0.234	2.500	Soje Complex

Sample Irradiation

The schemes for irradiation were performed with short and long irradiation times for radionuclides of short and long half-lives respectively [10]. For quality control, coal fly ash 1633b (NIST) reference material were irradiated in the two stages together with all the samples. For short irradiation, each prepared sample and standard were irradiated for two minutes at a neutron flux setting of 2.5×10^{11} n/cm²/sec in the outer irradiation channel (B4) outside the beryllium (away from the reactor core). A pneumatic transfer process (Rabbit type B) conveyed samples in and out of the reactor. For the long irradiation, samples were irradiated for six hours at a neutron flux setting of 5.0×10^{11} n/cm²/sec [6, 7] in the inner irradiation channel (B2) situated in the beryllium reflector (close to the core) and the Rabbit type A was used to transfer the samples in and out of the reactor core. After irradiations, the samples and standard together were ejected from the reactor to decay to an appropriate time.

Sample Counting

The counting schemes were also designed to measure emitted gammas from the irradiated samples resulting from the short and long irradiation. This procedure was carried out in a separate set-up which consists of a gamma-ray High Purity Germanium (HPGe) detector that is normally Pb-shielded to ensure safety of the analyst and the associated electronic components. The gamma-rays or signal from the samples detected were routed through the appropriate amplifiers and analog to digital converters to a computer based maestro-multichannel analyzer emulation software coupled to the detectors as its gamma-rays acquisition facility. The multipurpose gamma ray analysis software WINSPAN-2004 [8] was used for the peak identification and spectra evaluation.

For the short irradiated samples, the first short counts were performed immediately after irradiation and each of the samples and standards were counted for ten minutes. The second short counting was done after a decay period of two hours and the counting were performed for ten minutes each for both types of samples.

For the long irradiated samples, the first stage of counting was done after 2 to 3 days of decay and both type samples counted for 30 minutes each. The second stages of the counting were performed after nine days each type counted for sixty minutes.

The detector was calibrated in energy certified radioactive sources; ^{137}Cs emitting gamma-ray energy of 662KeV and ^{60}Co emitting two gamma-rays at 1172 and 1332.5 keV. Efficiency curve for the gamma-ray High Purity Germanium (HPGe) detector (ORTEC ©) Model number “GEM-30195” has been developed and published [9].

Spectra Analysis

The spectra which are plots of gamma-ray intensity versus energy (channel) were analyzed by calculating the area of each peak. The computer software WINSPAN-2004 was used for the peak identification and spectra evaluation and determination of the elemental concentration in the unknown sample with respect to the standard using the equation (1).

$$Conc_{sample} = \frac{Conc_{standard} \times Activity_{sample} \times weight_{standard}}{Activity_{standard} \times weight_{sample}} \quad (1)$$

Results and statistical analysis

In order to validate the analysis protocol, we compared results obtained for the standard Coal fly ash 1633b with the certified values. Results are presented in Table 2.

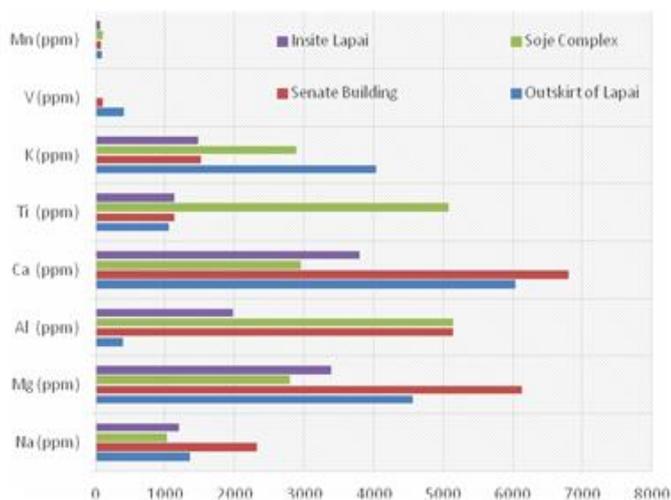
Table 2: Analytical results for the reference Material Coal Fly Ash 1633b

Elements	This work	Certified Values
Na (%)	0.185	0.201
Mg (%)	0.997	0.492
Al (%)	14.600	15.050
Ca (%)	1.410	1.510
Ti (%)	0.742	0.791
K (%)	2.019	1.950
V (ppm)	0260	295.600
Mn (ppm)	158.700	131.800

The concentrations of the eight elements identified from the sampling sites are shown in Table 3.

Table 3: Concentration of Elements in the Samples Identified

Elements (ppm)	Outskirt Lapai	Senate Building	Soje Complex	Inside Lapai
Na	1360 ± 02	2325 ± 03	1027 ± 15	1196 ± 02
Mg	4563 ± 06	6127 ± 09	2799 ± 44	3381 ± 07
Al	0399 ± 00	0510 ± 78	5146 ± 07	1973 ± 04
Ca	6038 ± 09	6799 ± 10	2949 ± 44	3794 ± 79
Ti	1058 ± 01	1138 ± 01	5076 ± 07	1136 ± 02
K	4030 ± 06	1510 ± 02	2890 ± 04	1477 ± 30
V	4055 ± 13	0098 ± 00	0010 ± 00	0018 ± 00

**Figure 1: Graphical interpretation of Statistical Parameters of Eight Elements Identified in all the Study Sites**

Discussion

Results presented in Table 2 for the standard Coal Fly Ash 1633b shows a great agreement between the obtained values with INAA and the certified values except for the magnesium which appears to be twice the expected value. This may be attributed to an error arising from (n, p) reaction on aluminum. Also the deviation observed in Vanadium and Manganese from analytical results of 260 ppm and 158.7 ppm with certified values of 295.6 ppm and 131.8 ppm respectively were within acceptable range.

From the results in Table 3, among the eight elements identified for the four sites, sodium ranges from 1027 ± 154 ppm to 2325 ± 35 ppm. From the four sites, the senate building and Inside Lapai (i.e. the T-Junction) have the highest mean concentration of Na and the possible source is mainly through incinerators and bush burning activities. Though sodium is a very essential element to all living organisms especially man

and fish. Thus, the exposure to moderate concentration of sodium is of health advantage.

The soil mineral, organic materials and fertilizer are possible sources of magnesium that were observed to have mean concentration in the four sites to range from 2799 ± 448 to 6127 ± 780 ppm. Both Senate building and the Outskirt of Lapai had the highest values of 6127±780 ppm and 4563 ± 69 ppm respectively. The high mean concentration in the Senate building and Outskirt of Lapai may be as a result of construction taking place as well as the direction of the movement of wind towards the sampling areas. Magnesium is an essential element to human health and exposure to a limit amount result to good health effect [10]

The mean concentration of aluminum in the four sampling sites ranges from 399 ± 6 ppm to 5190±780 ppm. The “Inside Lapai” and Soje complex have the highest (1973 ± 04 and 5146 ± 07 ppm respectively) which may be as a result of some anthropogenic activities taking place. However, to some considerable extent, Al is known to be non-toxic element. When one is exposed to high concentration of Al dosage, some health effect such as damage to the central nervous system, dementia, lung problems and loss of memory will be obvious.

For calcium being one of the major element and very essential and most abundant mineral in the human bodies, it accounts for approximately 1.5 % of the total body weight. It is an essential element for strong and healthy teeth and bone development in both children and adult. Deficiency of Ca in children may lead to rickets while in adults may lead to Osteomalcia or “softening of bone”. From Table 3, the mean concentration of calcium in the samples ranges from 2949 ± 443 ppm to 6038 ± 91 ppm. The samples collected from the Senate building and the Outskirt of the town recorded the highest concentration of Ca which may be as a result of the construction activities and wind direction movement, while Soje complex and Inside Lapai (T-Junction) recorded the lowest.

The mean concentration of titanium in the four sampling sites ranges from 1058 ± 16 ppm to 5076 ± 76 ppm as shown in Table 3 and Fig. 1. Again both Sanete building site and the Outskirt recorded the highest concentration due to the aforementioned reasons. Other possible sources of Ti in air are paint work and automobile. From Fig. 1 the range of V is 10 ± 001 ppm to 40 ± 60 ppm with sample from Outskirt having the highest value. The remaining three sites recorded relatively low concentration which may be as a result of wind movement.

Manganese in the four samples ranges from 61 ± 001 ppm to 8938 ± 13 ppm and Soje complex with Outskirt of Lapai recording the highest concentration which may be coming from anthropogenic activities such as bush burning, motor park activities, and welding activities. The Senate building and Inside Lapai (T-Junction) recorded the lowest concentration of Mn. This trace element is toxic in high concentration and may cause neurological problems.

Potassium in the four samples sites ranges from 1477 ± 78 ppm to 4030 ± 78 ppm. T-Junction and Outskirt records the highest concentration while Senate building and Soje complex records the lowest. The high concentration of K may be due to wood burning releasing particles of potassium into the atmosphere. Exposure to high concentration may also be toxic. However, K is an essential element required by the body for proper functioning of the body tissues.

Conclusion

In the troposphere, a significant portion of the aerosols particles are of anthropogenic origin. Since fogs are close to the

surface, they are affected by aerosols that are in the lower atmosphere close to their source of emission as the case of Inside Lapai (T-Junction) and Soje complex. The data collected within the four sampling sites shows that samples collected from Inside Lapai (T-Junction) and Soje complex have highest concentrations of Na, Mg, Al, Ca, Ti, V, Mn and K. This is undoubtedly attributed to the exhaust released from vehicles and heavy trucks passing through Suleja-Bida road and also some anthropogenic activities taking place such as welding activities, motor park garage activities, generators releases, wash-off from waste generated from mechanical workshop activities around the Soje complex and Inside Lapai. In Senate building and Outskirt of Lapai town, Vanadium and Manganese are little bit high due to the wind (North-Easterlies) movement transporting the air pollutants from different sources such as bush burning, and some other anthropogenic activities to the experimental sites. These aerosols particles identified in this work have an impact on the fog and cloud properties since they are characterized by the presence of haze particles "swelled" by picking up water.

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