Chapter Four

Experimental Work

4.1 Material and methods

This chapter deals with experimental aspects such as description of the area of study, soil sampling, and samples preparation.

4.2 Area of study

Nyala city is the capital of South Darfur state in the western part of the Sudan. It's located at elevation 2,208 feet (673 m) in Darfur region figure 3.1 [108]. Located at the intersection of longitude 24.53 degrees east and latitude 12.03 degrees north, It is important to note that this area is high density populated and tourisms area. The soil samples were dried, homogenized and sieved at 200 mesh grain size. Pressed powder pellets were prepared to avoid the elements contaminations, heavy metals and trace element analysis of samples by X-Ray fluorescence performed using X-ray fluorescence spectrometer Axios^{mAX} by PANalytical , This instrument is connected to a computer system using program for spectrometry. The trace elements concentrations are calculated from the program's calibration curves which were set up according to international reference materials, (standards). The detection limit is the lowest concentration, and it is function of the level of background noise relative to an element signal [109].The distance between each successive sample about one kilometer.

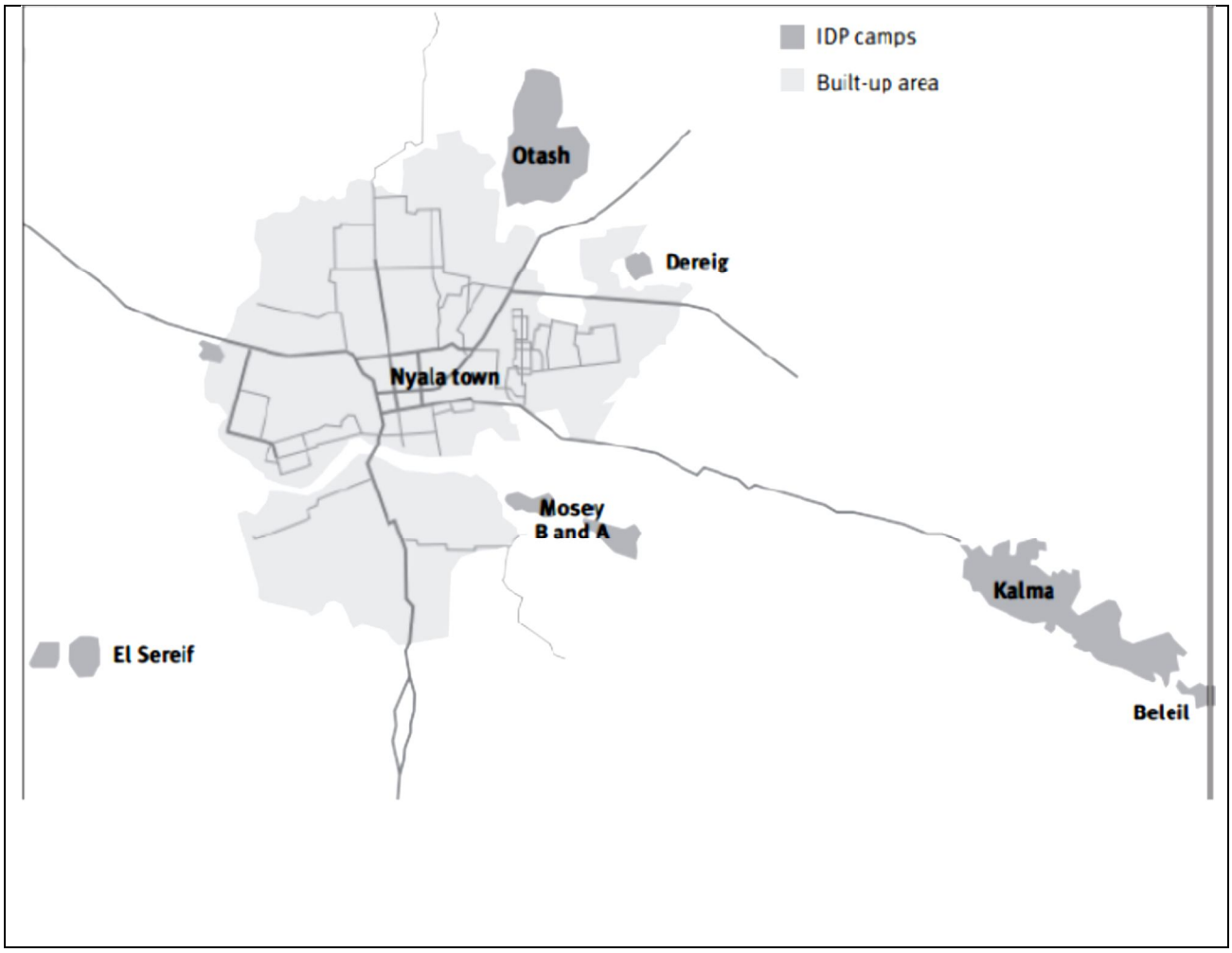

Figure 4.1: Map of Nyala city , South Darfur state, Sudan [108]

4.3 Sampling and Samples Preparation

Soil samples were collected from 40 locations in the area of the study, as shown in figure 4.1: samples were collected using the core method with a depth of about (0-5 cm). Two composite samples were collected from each location, one from subsurface land (inside) and the other one from surface land (outside). Samples were dried in open air dry place, mechanically crushed, and sieved through a 2 mm mesh sieve.

For x –ray florescence spectrometry, aliquot of each sample was transferred to a plastic container of 200gram capacity and sealed for about four weeks to reach secular equilibrium of radon, and their progenies [110]

Figure 4.2: sample sealed and transferred to a plastic container of 200g

4.4 Detection Limits

The detection limit is the fundamental limitation of a particular measuring system to distinguish a net signal from a background signal with a predetermined level of confidence. This limit is established as prior and is dependent upon the intrinsic instrument background and any reagent blank activity introduced in the chemical separation procedure. The detection limit is independent of the sample size or concentration of a radionuclide in the original material. Detection limits indicate our ability to measure activity with a particular system. With this limitation known, it is possible to estimate the necessary sample size to detect activity with a stated degree of confidence. In the development of a detection limit, the important factors are the instrument background, the reagent blank activity, the instrument detection efficiency, the chemical yield of the separated sample, and the time of the measurement.

4.5 Theoretical calculations

4.5.1 Dose assessment

The absorbed dose rate (nGy/h), and dose equivalent rate (nSv/h) in air one meter above the ground level at each location were calculated using the following equation [111].

$$D = R_K C_K + R_U C_U + R_{Th} C_{Th} \qquad (4.1)$$

Where D is the absorbed dose rate or dose equivalent rate, R_K, R_U, and R_{Th} are the conversion factors, expressed in nGy/h or in nSv/h per activity unit.

C_K, C_U, and C_{Th} are the concentrations of ^{40}K, ^{238}U, and ^{232}Th respectively expressed in Bq kg^{-1}.

The total uncertainty (σ_{tot}) of the calculated activities is composed of the counting statistical (σ_{st}) and weighted systematic error ($\sigma_{sys,i}$) calculated by the following formula [112].

$$\sigma_{tot} = \sqrt{\sigma^2{}_{st} + \frac{1}{3}\sum_1 \sigma^2{}_{sys,i}} \qquad (4.2)$$

The minimum detection limits of the setup for ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K were measured in Bq/kg.

The radioactivity activity concentration (A) of individual radionuclide for a peak at energy E in studied samples will be calculated as

$$\text{A } (BqKg^{-1}) = \frac{(N_{Ei})_{net}}{\in_{Ei} I_{Ei} tM} \qquad (4.3)$$

Where $(N_{Ei})_{net}$= net photopeak area at energy (E) of radionuclide i (counts), $(N_{Ei})_{net} = (N_{Ei})_S - (N_{Ei})_B$

A = specific activity concentration of individual radionuclide i for a peak at energy E in studied samples $(BqKg^{-1})$

N_S = total net counts at energy E of radionuclide i (counts),

N_B = background net counts at energy E of radionuclide i (counts),

$\in_{Ei}$= the photopeak detection efficiency of a particular γ-ray energy (E),

I_{Ei} = absolute intensity corresponding to the photo peak at energy (E),

t = counting time of the ceramic sample (s)

M = mass of sample (kg)

4.5.2 Internal and External Radiation Hazard Index

Radiation hazards due to natural radionuclide's of ^{40}K, ^{232}Th and ^{226}Ra (or ^{238}U) may be internal or external depending upon the location of a receptor indoor or outdoor. These hazards are defined in terms of internal or indoor

and external or outdoor radiation hazard index and are denoted by H_{in} and H_{ex}, respectively.

Assuming 370 Bq/kg of ^{226}Ra, 259 Bq/ kg of ^{232}Th and 4810 Bq/kg of ^{40}K produce the same gamma-ray dose rate, and limiting the external γ-radiation dose up to 1.5 mSv/y, a proposed "external hazard index (H_{ex})" has been introduced [113].

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \qquad (4.4)$$

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \qquad (4.5)$$

Where A_K, A_{Th} and A_{Ra} are the activity concentrations of ^{40}K, ^{232}Th and ^{226}Ra respectively.

The indoor hazard index is calculated to determine the radiation hazards from ^{40}K, ^{232}Th and ^{226}Ra.

4.5.3Gamma radiation hazard index

The γ-radiation hazard index ($I_{\gamma r}$) is a representative level index which is defined as [114].

$$I_{\gamma r} = \frac{A_{Ra}}{150} + \frac{A_{Th}}{100} + \frac{A_K}{1500} \qquad (4.6)$$

This index can be used to estimate the level of γ-radiation hazard associated with the natural radionuclides in specific materials. Values of index I ≤1 correspond to ≤ 0.3 mSv/y, while I ≤ 3 correspond to ≤ 1 mSv/y. To assess the radiological risk of the building materials used, it is useful to calculate the radium equivalent activity [115].

$$Ra_{eg} = (A_{Th} \times 1.43) + A_{Ra} + (A_K \times 0.077) \qquad (4.7)$$

Where A_{Ra}, A_{Th} and A_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, respectively.

4.6 Instrumentation and instrument set up

Measurement of radioactivity concentrations of the collected samples soil was carried out using x-ray florescence (XR).

4.6.1X-ray fluorescence spectroscopy

The X-ray fluorescence spectrometry (XRF) is an analytical screening tool that was first used to analyze lead (Pb) in paint in the 1970s during abatement and exposure studies [116].and has since been used in environmental testing of alloys, geological materials, sediments, glasses, with very minimal sample preparation and treatment [117].

Over the years, the XRF has gained acceptance from the environmental research community as a viable analytical tool because of the efficiency of the radioisotope source excitation coupled with extremely sensitive detectors and other electronics, hence offering multi element analysis capability, economy, high speed and simplistic operation, where its advantages and limitations are well comprehended. The introduction of this parts is to provide the basic concepts of the X-ray fluorescence and assess the performance of XRF.

4.6.2 Theory of the XRF analysis

The basics of the XRF lie in the atoms of the receiving sample emitting different energies when they are excited by X-rays. The excited photons enable the qualitative and quantitative analysis of most elements [118]. First the X-rays dislodge an atom from the inner shell. The atom from an outer shell fills the inner shell (K or L).

The excited atom releases energy in the X-ray region of the wavelength as it returns to the ground state. The released photons with energy are equivalent

to the difference between the two different shells. For instance, the transition from the L-shell to the K-shell results in a spectral line, which is designated k_α , while the transition from the M-shell to the K-shell provides a spectral line, which is designated K_β (Figure 4.3). Thus, each element possesses different characteristic lines in the spectrum because each type of orbital transition produces a distinct, X-ray [119].showed that when certain atoms are excited, they release energy in the form of fluorescence as they return to the unexcited state. The photons emitted are then detected by the instrument.

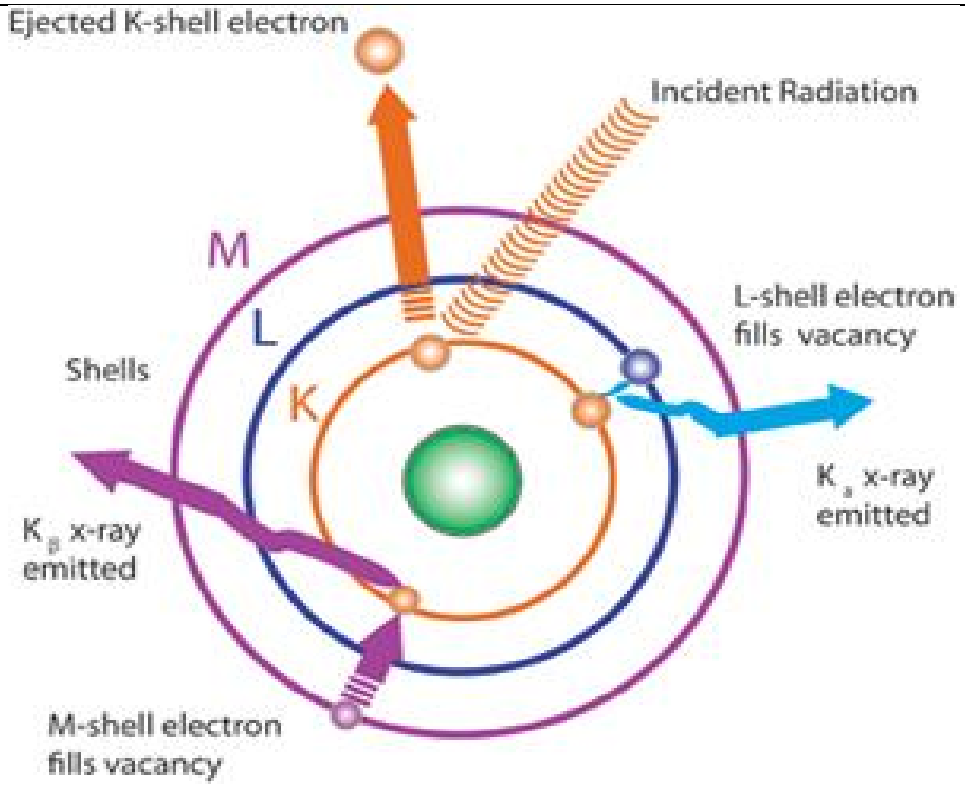

Figure 4.3:The three step process describing x-ray fluorescence,

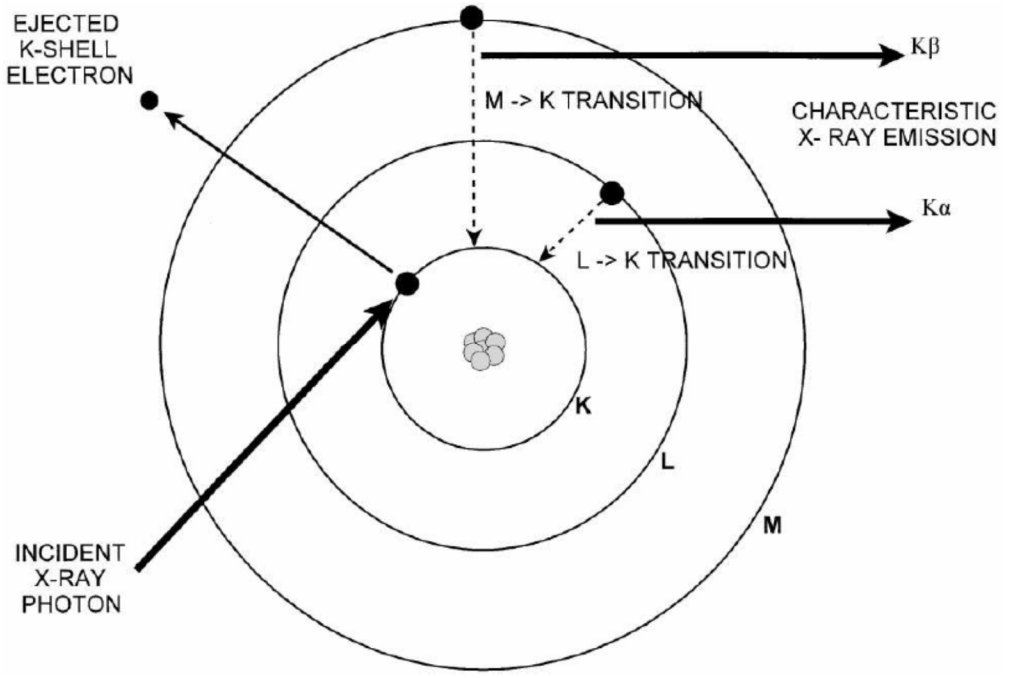

Figure 4.4: Mechanism of X-ray fluorescence of an atom

4.6.3 Selectivity

The XRF can be used to detect most of the elements in the periodic table ranging from Na to U and even higher atomic number (Z) elements, although the detection of low Z elements requires the use of a vacuum or helium purge gas [120].

Modern field portable XRF instruments, however, have improved solid state detectors with sufficient energy resolution for multi-element analysis with few spectral interference problems, and they do not require liquid nitrogen cooling. Many models have been developed and marketed for specific applications such as the analysis of Pb in paint [121].Under normal circumstances; a positive detection of a sample is confirmed by multiple fluorescence lines with different energy that can be expanded to show limited resolution of the analyzer (Figure 4.6). However, the interpretation

of the XRF spectra containing multiple fluorescence line overlaps can be very complicated due to the fundamental limitations of the detector in distinguishing photons with similar energies.

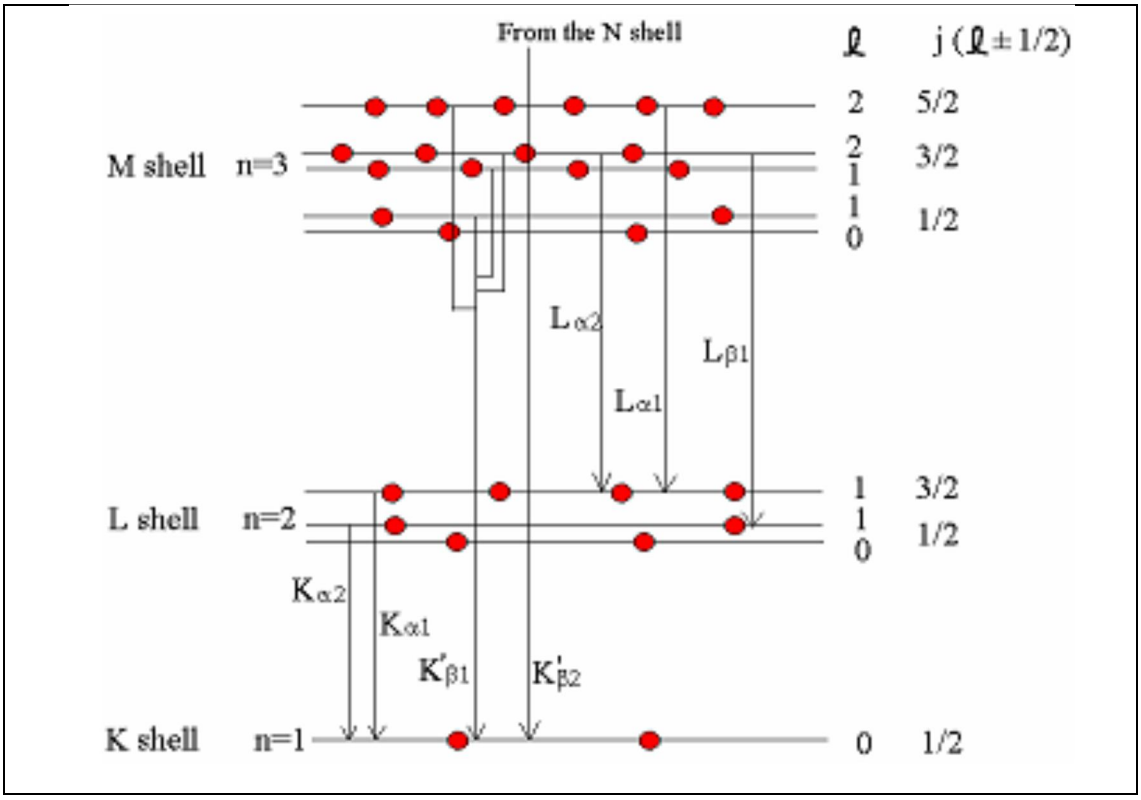

Fig 4.5: Electron transitions and emitted spectral lines in the atom after the K-shell ionization

4.6.4 XRF Sources

4.6.5 Radioisotope Sources

A variety of excitation sources may be used to irradiate a sample. Various radioisotope sources such as ^{55}Fe, ^{57}Co, ^{109}Cd, and ^{241}Am have been used, giving off radiation at a specific energy level. Because no single excitation source can efficiently excite the entire range of elements with different atomic numbers, two or three excitation sources can be used to

maximize the efficiency of the XRF detection on a wide range of concerned elements [122]. The analyzer emits primary radiation through which the sample being analyzed determines the intensity of the secondary (scattered) radiation. Based on its composition, thickness and density, the sample may absorb more or less of the primary-beam radiation. If the sample is small, thin, and low in density, it would allow much more of the radiation beam to escape, and the escaping radiation is known as the secondary (scattered) radiation [123].

There should always be a sample in contact with the measurement window when the x-ray tube is on. Individuals should never place any part of the body in the primary beam path as this may potentially lead to cancer. Therefore, caution should be taken when analyzing samples that are small and low in density.

4.6.6 X-Ray Tube Source

High power x-ray tubes are another alternative source of the XRF, and also often associated with laboratory XRF instrumentation, which results in a higher sensitivity (Figure 4.7).The handheld XRF spectrometry system needs to be confirmed by the laboratory analysis because the laboratory-based XRF requires sequential extraction of heterogeneity of the sample and higher energy source. Low-power X-ray tubes (1-50W) are sometimes considered to be a qualitative tool [105].

But it depends upon the analysis and calibration whether the analysis is qualitative or quantitative. In spite of a number of advantages aforementioned, the short half-life of the XRF sources have implications for the instrument's sensitivity. Thus, the sources needed to be replaced when

the sensitivity is reduced. Calibration standards are thus mandatory and units may require servicing after two years [124].

4.7 Experimental setup

Figure 4.6 shows the arrangement of a typical X-ray fluorescence spectroscopy experiment which includes a source of primary radiation (an X-ray tube), the sample whose X-ray spectrum is studied and an equipment to detect the secondary X-rays (X-ray detector) and to acquire and record the spectrum (acquisition and processing system).

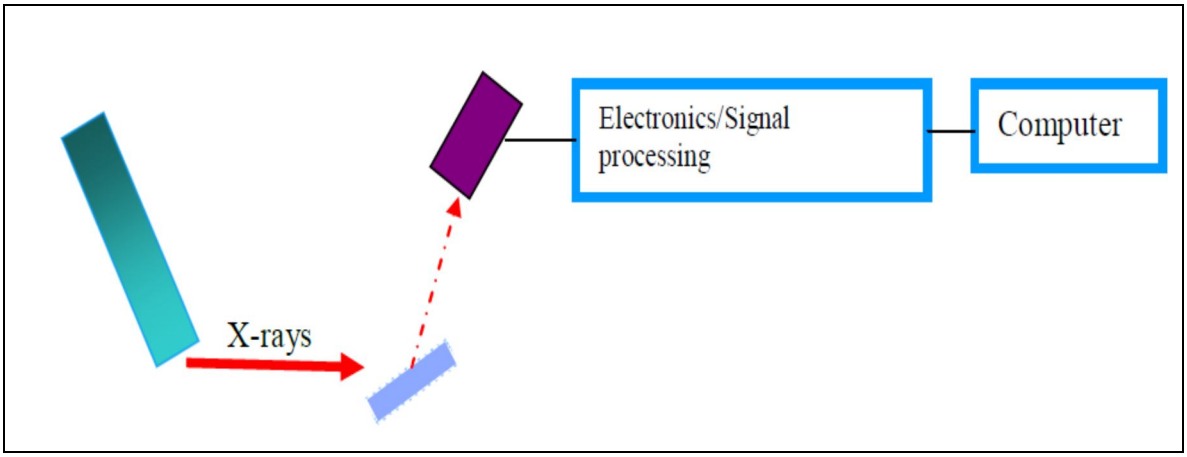

Figure 4.6: Scheme of the arrangement of the experimental setup for XRF

4.7.1 X-Ray Fluorescence (XRF) Spectrometer by PANalytical

The Axios^{mAX} X-ray fluorescence XRF spectrometer by PANalytical is designed to meet the most challenging process control and research and development applications. The instrument comes with innovative features and high-quality design. It incorporates the SST-max x-ray tube, which is designed for ultimate close coupling, integrates ZETA Technology, and practically eliminates instrument drift.

The main features of the Axios^{mAX} X-ray fluorescence XRF spectrometer are:

a. High throughput design.
b. Non destructive, precise and reproducible XRF elemental analysis across the periodic table.
c. Reliable, zero-drift performance over the lifetime of the X-ray tube.
d. Maximum instrument uptime for consistent process control.
e. high speed and excellent sensitivity in light element analysis with Axios max advance.

The Axios is a low power (1 kW) wavelength dispersive XRF (WDXRF) spectrometer built on the proven and robust Axios instrument platform. It is designed for entry level applications where the precision of WDXRF is needed but sample throughput is low. The Axios offers the convenience of an internal cooling system that removes the requirement of an external chiller needed for higher power systems. Designed with customers needs in mind, the system is engineered to be extremely quiet, dust resistant and thermally stable despite the air cooling of the tube and cabinet. Incorporating proven SST tube technology the system is capable of achieving an output of 20-60 kV and 10-50 mA making it the highest performance 1 kW spectrometer available. Able to achieve the same accuracy and precision of higher power spectrometers, the Axios 1 kW system is an ideal choice for customers requiring high performance and who do not want the inconvenience of a water chiller [122,123].

Figure 4.7: X-Ray Fluorescence Spectrometer by PAN alytical-Laboratory XRF Analyzer.

4.7.2 Factors Affecting XRF Calibration

Especially for quantitative analysis, XRF methods require calibration of the XRF analyzer with standards of known concentrations.The calibration simply compares the X-ray intensity of the elements of interest to the certified, known concentrations of a type of sample (e.g. solids, liquids, and films). During a calibration procedure the following factors, which may influence the accuracy and precision of the method, should be considered:

a) detector resolution and relationship to the spectral inferences;
b) sample matrixes;

c) Accuracy and suitability of standards; and sample morphology (i.e. uniformity, water content, particle size distribution and surface condition) and sample measurement geometry [125].

These limiting factors can be addressed so that an appropriate and meaningful calibration can be done. Different detectors have different efficiency to resolve overlapped X-ray spectral lines. For example, overlapping lines between As-K and Pb-L might not be well separated by certain detectors, resulting in analytical error. Matrix effects occur when other elements interfere with the target element, and this interference can have an impact on the measured X-ray intensity of the target element. These effects produce a non-liner intensity response versus target element concentration, and they appear as either X-ray absorption or enhancement phenomena. These effects can be corrected when the XRF analyzers are calibrated. Moreover, the standard concentrations should have accurate concentrations of those elements of interest to be analyzed with a suggested time measurement. Also, the standard should exhibit the same texture as the sample to be analyzed in order to have an accurate calibration method. It is well documented that the sensitivity of the XRF decreases as the distance between the sample being analyzed and the excitation source increases. This discrepancy can be reduced by maintaining the same measurement geometry between all calibration standards and sample measurements. For best results, the window of the probe should be in direct contact with the sample[126].

4.8 Effects of Particle Size

The XRF analytical method has been demonstrated on different chemical composition of all kinds of materials.

The materials can be in solid, liquid, powder, filtered or other form. However, particle size in solid samples can influence the XRF accuracy.

For example [108], reported that the sensitivity of an XRF measurement goes down as the sizes and densities of the particles increase, because the X-ray absorption losses increase. Similarly, found that particle size effect in XRF showed a clear decrease in the XRF intensities when these were observed with larger particle size [128]. Both studies reported that correction can be made. In regard to metal distribution at different particle size fractionations, it is well documented that finer particles tend to preferentially adsorb metals and be associated with higher metals concentrations [129].

4.9 Moisture Interference

Sample moisture can affect the accuracy of the analysis. It was reported that sample moisture as much as 20% can affect the analysis [111]. So, soil and sediment samples should be routinely dried to remove all matrix moisture when the water content exceeds 20%. Limiting factors that affect the XRF performance capability include sensitivity of instrumental techniques; low concentration of element of interest; interference of other elements in the matrix; and using large volume of water as representative samples [131].

4.10 Sediment as Toxicity Indicator

It is well documented that sediment samples are a good indication of environmental concern with respect to metal contamination of anthropogenic activities and natural geological processes [132].Anthropogenic sources such as agriculture; mining and urban systems can transport chemical pollutants in to waterways and sewer systems, which in turn discharge into natural waterways. Due to less variability with respect to spatial and temporal scale than water, sediment samples provide a reliable, consistent indication of

toxicity and also can concentrate chemical contaminants up to several orders of magnitude [133].

Chemical toxicity accumulates over a long temporal scale and is not self-purified by water, and can enter biological food chains[134].

4.11 Adverse Effects of Exposure to Metals

A metal such as Pb is used in many different ways in the production of batteries, pipes, gasoline, paints and household products. The long-term exposure effects to Pb may include decreased performance of the nervous system, weakness in fingers, ankles and anemia .Likewise, exposure to As may result in abnormal heart rhythm, decreased production of red blood cells, nausea and, if at a concentration as much as 200 μg/day, possible bladder cancer [135] .Elemental Zn and Cu are not as toxic as Pb, As, Hg or Cd. Only low concentrations of As, Hg or Pb can cause severe damage to the nervous and the renal system because these are cofactors, promoters and initiators in many diseases and cancer [136].Contamination in soil by metals is of major concern because they can impair productivity and soil structure and reported that metals in sediment reduce microbial enzymatic activity in soil, which in turn influences vegetation growth and production, as well as the micro flora community[137].

Metals that are deposited in soil as described in a study carried out [138].

in the Danube River, Montenegro can bio accumulate in living tissues of biota, and thus influence the distribution of density of the organisms and their community.

Although there are no data available regarding the adverse physiological effects on the residents living around Nyala city, there is scientifically valid

vidence suggesting that consumption of highly contaminated food stuffs and elevated exposure to such metals can potentially have adverse health effects. There are general agreements and evidence that suggest inorganic metals bioaccumulation in vegetables and fish could cause damage to the central nervous system (CNS) and reproductive fertility, thereby affecting the development, behavioral, and reproduction characteristics, particularly in children [139]. Moreover, a metal like Pb is a potent inhibitor of heme synthesis, which is necessary for the function of red blood cells, and methyl mercury, an organic form of Hg, has been well documented in cases of the central nervous system deterioration due to the damage of the micro tubules [140].