

**SPECIATION OF SOLUBLE TITANIUM (Ti) AND VANADIUM (V) IN  
AGRICULTURAL DRAINAGE WATER AND AQUEOUS SOIL SEDIMENT  
EXTRACTS USING FLAME ATOMIC ABSORPTION SPECTROMETER  
(FAAS)**

**BY**

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TECHNOLOGY.**

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**CERTIFICATION**

This is to certify that **IDOKO, MESHACH O.** with Registration Number **FPI/ND/SLT/14/017**, a National Diploma (ND) student in the Department of Science Laboratory Technology has satisfactorily completed his project work as part of the requirement for the award of National Diploma (ND) certificate.

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## DECLARATION

I declare that this project report entitled Speciation of soluble Titanium (Ti) and Vanadium (V) in agricultural drainage water and aqueous soil sediment extracts using Flame Atomic Absorption Spectrometer (FAAS)” was performed in the department of Science Laboratory Technology under the supervision of Mr. Edmund Okorie. The information derived for the literature was duly acknowledged in the text and a list of references is provided at the end of the report. This report was not previously presented for a certification, diploma or degree in any higher institution.

.....

Name of Student

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Signature

.....

Date

## **DEDICATION**

This project work is dedicated to my Holy Father, precious Saviour, and beloved Friend for His unfailing love and everlasting faithfulness in my life.

## ACKNOWLEDGEMENT

My undying appreciation goes to God Almighty for granting me the privilege and opportunity to be educated in all facet of life.

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## **ABSTRACT**

*This work was carried out to check the concentrations of Titanium (Ti) and Vanadium (V) metals in agricultural drainage water and aqueous soil sediment extracts from Tony farms limited Koton-karfe Local Government Area, Kogi State. The average concentrations of Ti and V were 19.88 $\mu$ g/g and 12.99 $\mu$ g/g respectively in the aqueous soil sediment extracts and 25.98ppm and 25.25ppm respectively in the agricultural drainage water. This result showed that the drainage water and soil sediment of this area is heavily polluted.*

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# CHAPTER ONE

## 1.0 INTRODUCTION

### 1.1 Background of Study

Contamination of the surface of the earth by metallic contaminants from human activities has been significant (Markham, 1994) and thus, regimes of ecosystem of the aquatic and terrestrial environment of the earth's surface are burdened with a range of metallic pollutants/contaminants. For example, many materials were processed in significant quantities to support the developing technologies underpinning the growth of the developed countries (Markham, 1994; Macklin, 1992). The extraction and utilization of metals as major components of infrastructure and in high value goods became the cornerstone of the development of human civilization (Wedepol, 1991).

Through human activities, contamination of the Earth's surface by metallic contaminants developed from localized problems associated with mining and initial ore processing, example like the Zamfara lead (Pb) poisoning in northern Nigeria (WHO Lead NGR, 2010), through to large scale manipulation and refining, construction, manufacture and finally to waste disposal. This, coupled with the focusing of population center into industrialized cities, resulted in an increased burden on the environment (Lowe and Bowlby, 1992). The consequence of this has increased awareness of human and industrial impacts on environmental systems at the local and global scale. This has resulted in efforts to manage and improve the degraded quality of aquatic and terrestrial systems (Ozbes *et al.*, 2011; Thornton, 1996; Cairney, 1995; Bora, 1998).

The increase in human stress on sensitive surface environments requires the development of reliable management options for soil and water systems, which are often contaminated with a mix group of physical and, chemical components. Contamination from

processing residues, direct deposition and accidental releases of organic and metallic species create a wide spectrum of environmental hazards (Hagelstein, 2009; Cairney, 1995; Ferguson *et al.*, 1998). An in-depth understanding and appropriate remediation of these situations would rely on an intimate mix of science, technology and socio-economic factors (Haruna *et al.*, 2013).

It is within this context that the speciation of metallic contaminants provides both the potential hazard (mobility, reactivity, toxicity) (Centeno, 2003) and thus, the pathway to a technological acceptable solution (remediation option). The factors influencing the speciation and changes with both time and environmental conditions provide the greatest challenges and opportunity for environmental science and technology (Haruna *et al.*, 2013).

Within the terrestrial ecosystem, soils play a major role in element cycling and accumulate heavy metals in concentration orders of magnitude higher than in water and air (Ashraf *et al.*, 2012).

It is widely recognized that to assess the environmental impact of soil pollution, the determination of the metal speciation will give more information about the potential for release of contaminants and further derived processes of migration and toxicity (Rauret *et al.*, 1988; Usero *et al.*, 1998). Therefore, in geo-environmental studies of risk assessment, chemical partitioning among the various geochemical phases is more useful than measurements of total heavy metals contents (Campanella *et al.*, 1995; Quevauviller *et al.*, 1996). Among the procedures to determine element speciation, those based on sequential extraction are the most widely used (Usero *et al.*, 1998). These works are of interest in environmental studies to inform on the interactions with other components of the biosphere as well as to outline areas of potential toxicity and to provide information on the soil micronutrient levels for agricultural use (Wilcke *et al.*, 1998). To assess the binding of heavy

metals to the main fractions in soils, a five – step sequential extraction procedure based on the capacity of some extracting reagents to remove the heavy metals retained from the geochemical phases has been used (Tessier *et al.*, 1979).

Heavy metals take place in biogeochemical cycles and are not permanently fixed in soils; therefore, assessment of their distribution in soils is a key issue in many environmental studies. Heavy metals are included in soil minerals as well as bound to different phases of soil particles by a variety of mechanisms, mainly absorption, ion exchange, co-precipitation, and complexation. Moreover, soil properties such as contents of organic matter, carbonates, oxides as well as soil structure and profile development influence the heavy metal mobility. The knowledge of the binding of metals with the different soil phases and components is of major interest to assess the connections with other biotic and abiotic elements of the environment (Ashraf *et al.*, 2012).

Heavy metals are classified as metallic elements that have relatively high atomic weight and are poisonous at low concentrations. They are natural components of the earth crust and they cannot be degraded or destroyed (Lentech, 2011). Living organisms require trace amount of some heavy metals such cobalt, copper, manganese, vanadium, molybdenum, iron and strontium for metabolic process, but in excess, these metals can also be detrimental to the organisms (Science Daily, 2012).

Heavy metals can enter a water supply through pollution of industrial and consumer wastes or even from acidic rain breaking down soils and releasing heavy metals into streams and ground water (Lentech, 2011). Heavy metals or chemical elements are easily introduced into aquatic system as a result of chemical weathering of soil and rocks from volcanic eruptions and from a variety of human activities involving processing or using of metals and substances that contained metals. There are two different types of sources of pollutants in our

water bodies, namely: point source and non-point or diffuse source. Point source is a localized pollution where pollutants come from single identifiable sources. The second type of pollution sources are non-point or diffuse sources, where pollutants come from dispersed sources and often difficult to identify sources (Lentech, 2006).

Water pollution occurs in various forms and is caused by different factors. The major causes of water pollution in most countries in the tropics can be linked to human activities such as sewage and refuse disposal, industrial effluents, agricultural activities, mining and quarrying activities. The most common source of water pollution in developing nations is domestic sewage and refuse (Butu and Iguisi, 2013).

Several other studies have also shown that a considerable number of chemical elements are leached from refuse dumps during raining season into ground water and streams (Olofin, 1991). Farouk (1997) opines that mechanic workshops, where used engine oil and petrol are continually discarded are also available sources of metallic contaminant. Industrialization is another major source of chemical pollution; industrial effluents are discharged into water sources without treatment. Modern agriculture is now becoming a nuisance to mankind. The insecticides, pesticides, chemical fertilizers especially nitrate and phosphate are used annually to boost agricultural production and these chemicals are washed down the soil by rain and eventually end up to contaminate the ground and stream water ways (Butu and Iguisi, 2013).

In most river basins diffuse sources contribute a very large portion of dissolved load carried by mainstream channel. Example of diffuse or non-point source include sediment from erosion, acid from mine and drainage from urban or industrial areas. In urban areas pollutants transport to receiving water bodies is usually through well defined system of combined or separate storm sewers. The pollution of water resources from these different

sources would have remarkable effect on aquatic biota through addition of biodegradable materials in solutions or suspension and toxic chemical substances as well as general environmental effects on the portability of water. Heavy metals are known to be carcinogenic and fatal, they are generally dangerous to living organisms especially man because of their bioaccumulation nature, they accumulate in living tissues anytime they are taken up and stored faster than they are metabolized or excreted (Lentech, 2011).

Heavy metals discharged in aquatic systems may be immobilized within the stream sediments by main processes such as adsorption, flocculation and co-precipitation. Therefore, sediments in aquatic environment serves as a pool that can retain or release heavy metals to the water column by various processes of remobilization. Several studies have demonstrated that the concentration of metals in sediments can be sensitive indicator of contaminants in aquatic systems (Butu and Iguisi, 2013).

Titanium, symbol Ti, silver-white metallic elements used principally to make light, strong alloy. Titanium is one of the transition elements of the periodic table (Periodic Law). The atomic number of titanium is 22. The metal is extremely brittle when cold, but is readily malleable and ductile at a low red heat. Titanium melts at about 1668°C (about 3034°F), boils at about 3287°C (about 5949°F) and has a specific gravity of 4.5. The atomic weight of titanium is 47.87. It ranks ninth (9<sup>th</sup>) in abundance among the elements in Earth's crust but is never found in the pure state. It occurs as an oxide in the minerals ilmenite, FeTiO<sub>3</sub>; rutile, TiO<sub>2</sub>; and sphene, CaO.TiO<sub>2</sub>.SiO<sub>2</sub> (Redmond, 2008).

Because of its strength and light weight, titanium is used in metallic alloys and a substitute for aluminum. Alloyed with aluminum and vanadium, titanium is used in aircraft for firewalls, outer skin, landing-gear components, hydraulic tubing, and engine supports. The compressor blades, disks and housings of jet engines are also made of titanium. Titanium

is also widely used in missiles and space capsules. The relative inertness of titanium makes it available as a replacement for bone and cartilage in surgery and as a pipe and tank lining in the processing of foods. It is used in heat exchangers in desalinization plants because of its ability to withstand salt water corrosion. In metallurgy, titanium alloys are employed as deoxidizers and denitrogenizers to remove oxygen and nitrogen from molten metals. Titanium dioxide, known as titanium white, is a brilliant white pigment used in paints, lacquers (fast drying liquid applied to surfaces of objects to provide a decorative, stiffening, or protective coating), plastics, paper, textiles, and rubber (Redmond, 2008).

Vanadium, symbol V, silver-white metallic element with an atomic number of 23. Vanadium is one of the transition elements of the periodic table (Periodic Law). Vanadium takes a high polish and is one of the hardest of all metals. It melts at about 1910°C (about 3470°F) boils at about 3407°C (about 6164°F), and has a specific gravity of 6.11. The atomic weight of vanadium is 50.94. Vanadium ranks about nineteenth (19<sup>th</sup>) in abundance of the elements in Earth's crust. It is never found in the pure state, but occurs in combination with various minerals throughout the world. Some of these vanadium ore minerals include roscoelite,  $K(V^{3+},Al,Mg)_2(AlSi_3O_{10})(OH)$ , vanadinite,  $Pb_5(VO_4)_3Cl$  and carnotite  $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$  etc. (Redmond, 2008).

Because of its hardness and great tensile strength, the metal is used in many alloys such as ferrovanadium, nickel vanadium, and chrome-vanadium. Chrome-vanadium steels are used in the production of springs and in transmission gears and other engine parts. Titanium vanadium alloys are used for missile cases, jet-engine housings, and nuclear-reactor components. As a catalyst, vanadium has largely replaced platinum in the manufacture of sulfuric acid and is employed widely as a photographic developer, as a reducing agent, and as a drying agent in various plants (Redmond, 2008).

Speciation is defined as the identification and quantification of the different, defined species, forms, or phases in which an element occurs and is essentially a function of the mineralogy and chemistry of the soil sample examined. Quantification is typically done using chemical solutions of varying but specific strengths and reactivity to release metals from the different fractions of the examined soil (Ashraf *et al.*, 2012).

Many analytical techniques have been developed for chemical speciation of elements in the environmental samples: typically – sequential leaching methods, hyphenated techniques such as GC-ICP-MS (analysis of organometallic elements) and x-ray spectroscopic techniques. These methods of analysis provide significant information on the chemical forms of elements in the environment in terms of analysis, it is possible to identify and quantify species in environmental samples (Haruna *et al.*, 2013). This project work used the flame atomic absorption spectrometer (FAAS) for its speciation process.

Atomic absorption spectroscopy is a spectro-analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. This technique is used for determining the concentration of the particular element (the analyte) in a sample to be analyzed (Wikipedia, 2016).

## **1.2 Aims and Objectives**

The main purpose of this project is to determine the concentrations of Titanium (Ti) and Vanadium (V) in agricultural drainage water and aqueous soil sediment extracts.

## **1.3 Significance of the Study**

Total metal concentration is a good indicator of the degree and extent of contamination (Tessier *et al.*, 1979). It is use in assessing the potential effect of soil sediment contamination, this implies that all forms of a given metal have an equal impact on the environment (Jaradat, 2006).

Heavy metals cannot be destroyed by biochemical processes; hence to evaluate the environmental impact of contaminated soil, knowledge of the total concentration of metals is insufficient without considering their speciation (Lo and Yang, 1998; Kirpichtchikova, 2006; Asagba *et al.*, 2007).

#### **1.4 Scope of the Study**

This study focuses on the determination of the levels/concentrations of species of soluble titanium (Ti) and Vanadium (V) in agricultural drainage water and aqueous soil sediment extracts using flame atomic absorption spectrometer (FAAS) which is an indication of possible environmental pollution risks.

#### **1.5 Description of the Study Area**

The site of this study is an irrigable farm land in Tony farms limited located in Koton-Karfe Local Government Area of Kogi State, North Central, Nigeria. The farmland has a sandy-clay soil type and is bounded by a river called Enyogi (black river). The waste water discharge from the farm is let into the black river which is tributary of river Niger.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 Definition of Chemical Speciation

The determination of distinct chemical species often referred to as speciation analysis is now widely acknowledged to be of vital importance in environmental chemistry. The term chemical speciation may encompass both functionally defined speciation, i.e. the determination of species that are, for example, available to plants or present as exchangeable forms and operationally defined speciation which refers to the determination of extractable forms of an element. While it is often possible to define a particular compound or oxidation state when dealing with solutions, for example, natural waters, it is far more difficult to characterize the actual chemical form of an element in solids such as soils and sediments. Thus, speciation tends to be defined somewhat differently by research workers to reflect their field of study. However, one of the most comprehensive formal definitions of speciation is the one recommended by the International Union of Pure and Applied Chemistry (IUPAC), which states that speciation is the process yielding evidence of atomic or molecular form of an analyte (Lobinski and Szpunar, 1999). As such, this definition was subsequently elaborated conspicuously as the specific form of an element defined as to electronic or oxidation state, complex or molecular structure and isotopic composition (Templeton *et al.*, 2000). In addition, International Union of Pure and Applied Chemistry (IUPAC) has recently evaluated and provided a definition of speciation as an analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample; the chemical species are specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure; the speciation of an element is the distribution of an element amongst defined chemical species in a system

(Clough *et al.*, 2012). With this elaboration, chemical speciation has now clearly demarcated itself from chemical fractionations, which were previously interchangeable and confusing.

The determination of such specific chemical entities is of course not new to analytical chemists. For example, the determination of  $\text{NO}_3$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , and  $\text{NH}_3$  where the nitrogen is characterized into its most environmentally important forms is long established (Hill, 1997). However, the characterization of metallic contaminants does not have the same history, although with the increased awareness of the importance of chemical speciation in terms of toxicity, mobility, bioavailability reactivity and persistence in the environment, a range of sensitive yet specific analytical techniques have now been developed to address a wide range of environmental complex problems.

## 2.2 Analytical Approaches to Speciation Studies

Many analytical techniques have been developed for chemical speciation of elements in the environmental samples: typically, sequential leaching methods (Koschinky and Hein, 2003), hyphenated techniques such as GC-ICP-MS (analysis of organometallic elements) (Hirata *et al.*, 2006), X-ray spectroscopic techniques (Ohnuki *et al.*, 2005). These methods of analysis provide significant information on the chemical forms of elements in the environment (Hirose, 2006). In terms of analysis, it is possible to identify and quantify species in environmental samples. Speciation studies on environmental samples were initially focused mainly on separation of specific elemental species or groups of species (Ebdon *et al.*, 1987; Harrison and Rapsomaniskis, 1989). Species separation is achieved mainly by one of the following well known techniques: liquid chromatography (LC), gas chromatography (GC), capillary electrophoresis (CE), and gel electrophoresis (GE) (Hill, 1997). The choice is determined by the chemical properties of the species, the available skills and infrastructure in the laboratory, and last but not the least, the available resources.

However, during the last two decades substantial progress was made in incorporating separation method with powerful detection methods for reliable quantitative measurements. Majority of work performed coupling GC with atomic spectrometry has so far been achieved using flame spectrometry as a detector (Webster and Karmahan, 1992). This approach has been used most commonly for analytes that are present in relatively high concentration; example, determining organo-lead species in fuel or roadside dust (Hill, 1997). A potential limitation of using GC is that often the sample must be derivatised to make it volatile enough for analysis. This can greatly increase sample preparation time, which may cause loss of analyte and uncertainty about the identity of the original species in the sample. To deal with such problems, high performance liquid chromatography (HPLC) is one of the most common methods used for separation of non-volatile analytes and has been extensively coupled to atomic spectroscopy for quantification. There are a large number of resin supports that are being in use as the stationary phase with anion exchange, cation exchange, size exclusion, chelating and reversed phase, e.g. octadecylsilane which is often used in conjunction with an ion pairing reagent such as tetrabutylammonium phosphate, diethyldithiocarbamate or 8-hydroxyquinoline to enhance separation of analytes. In this way, analytes with different oxidation states e.g.  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  are separated and quantified (Peter, 2001). In the same vein, arsenic has been suspended into  $\text{As}^{3+}$ ,  $\text{As}^{5+}$ , monomethyl arsenic acid, dimethyl arsenic acid and arsenobetaine using an anion exchange resin with an ammoniacal potassium sulphate mobile phase (Hill, 1997; Ebdon *et al.*, 1987). In addition, the HPLC separation of arsenic species has been coupled with online microwave digestion and hydride generation to facilitate the direct determination of reducible and non-reducible forms of arsenic (Ure and Davidson, 1995). The other convenient method for on-line coupling are inductively coupled plasma atomic emission spectrometry (ICP-AES), which sometimes referred to as ICP-Optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry

(ICP-MS). ICP-MS has enabled multi-elemental detection, isotopic discrimination with extremely high sensitivity. Moreover, HPLC and GC were successfully coupled to ICP-MS and now referred to as hyphenated techniques for speciation analysis. This technique is now the most frequent used analytical techniques for speciation purposes. For instance, Fan *et al.*, (2012) determined the concentration of Cu and its chemical forms in soil extracts using inductively coupled plasma optical emission spectrometry (ICP-OES).

Similarly, electroanalytical method, for example, anodic stripping voltammetry (ASV) and other electroanalytical techniques such as amperometry potentiometry have also been applied for quantification of the various oxidation states of an element. ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{Cr}^{6+}/\text{Cr}^{3+}$ ,  $\text{Tl}^{3+}/\text{Tl}^{4+}$ ,  $\text{Sn}^{4+}/\text{Sn}^{2+}$ ,  $\text{Mn}^{4+}/\text{Mn}^{2+}$ ,  $\text{Sb}^{5+}/\text{Sb}^{3+}$ ,  $\text{As}^{5+}/\text{As}^{3+}$  and  $\text{Se}^{6+}/\text{Se}^{4+}$ ) its organometallic species, or metal complexes (Harrison and Rapsomaniskis, 1989; Caroli 1996, Quevanviller and Maier, 1994).

Of recent, various mathematical modeling and computer aided programs have been developed for speciation analysis. For example, in many studies in which metal speciation in soil solution is connected to metal uptake by target organism, the Free Ionic Activity Model (FIAM) was used (Campbell, 1995). This model was later extended into the Biotic Ligand Model (BLM) in order to include the influence of competing cations like  $\text{Ca}^{2+}$  and  $\text{H}^{+}$  (Di-Toro *et al.*, 2001). With more advances in this aspect, Donnan Membrane Technique (DMT), Diffusive Gradient in Thin films (DGTs) have been developed and successfully applied in speciation analysis. Similarly, Windermere Humic Aqueous Model (WHAM VII) is the latest version of the mathematical model and computer aided program, which is developed and thus world widely embraced (Tipping, 1998). The WHAM VII model contains database for cation binding to humic and fulvic acids, including all rare earth elements and silver. It stimulates the precipitation of iron(III) and aluminium hydroxides, and binding of ions to precipitate.

The binding activity of dissolved organic matter is used to generate distributions of predicted free ions concentrations (Lofts and Tipping, 2011).

### 2.3 Selection of Fractions

In defining the desired partitioning of trace metals, care was taken to choose fractions likely to be affected by various environmental conditions; the following five fractions were selected.

**Fraction 1. Exchangeable.** Numerous studies performed on sediments or on their major constituents (Clays hydrated oxides of iron and manganese, humic acids) have demonstrated the adsorption of trace metals; changes in water ionic composition (e.g., in estuarine waters) are likely to affect sorption-desorption processes.

**Fraction 2. Bound to Carbonates.** Several workers have shown that significant trace metal concentrations can be associated with sediment carbonates; this fraction would be susceptible to changes of pH.

**Fraction 3. Bound to Iron and Manganese Oxides.** It is well established that iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions (i.e., low Eh).

**Fraction 4. Bound to Organic Matter.** Trace metals may be bound to various forms of organic matter: living organisms, detritus coatings on mineral particles, etc. the complexation and peptization properties of natural organic matter (notably humic and fulvic acids) are well recognized as is the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters organic matters can be degraded, leading to a release of soluble trace metals.

**Fraction 5. Residual.** Once the first four fractions have been removed, the residual solid should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature (Ashraf *et al.*, 2012).

## 2.4 Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometry (AAS) is an analytical method for quantification of over 70 different elements in solution or directly in solid samples. Procedure depends on atomization of elements by different atomization techniques like flame (FAAS), electrothermal (ETAAS), hydride or cold vapour. Each atomization techniques has its advantages and limitations or drawbacks. A comparison of several AAS techniques is given in

Table 1.

	FAAS	GFAA	Hydride Generation AAS	Cold Vapour AAS
Elements	68	50	As, Se, Sb, Bi, Pb, Sn	Hg
Limit of Detection	+	++++	+++	++++
Precision	++++	+	+	+
Interferences	+++	+	++++	++++
Analysis Time	++++	+	++	++
Sample Preparation	+++	+++	++	++
Operation Skills	+++	++	++	++
Operation Costs	++++	++	++	++

+Bad, ++Moderate, +++Good, ++++Very Good

Table 1. Comparisons of AAS techniques.

(Asli *et al.*, 2013).

Two types of flame are used in FAAS: (i) air/acetylene flame, (ii) nitrous oxide/acetylene flame. Flame type depends on thermal stability of the analyte and its possible compounds formed with flame concomitants. Temperature formed in air-acetylene flame is around 2300°C whereas acetylene-nitrous oxide (dinitrogen oxide) flame is around 3000°C

(Skoog *et al.*, 1998). Generally with air/acetylene flame antimony, bismuth, cadmium, calcium, caesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin and zinc can be determined. On the other hand for refractory elements such as aluminium, barium, molybdenum, osmium, rhenium, silicon, thorium, titanium, and vanadium, nitrous oxide/acetylene flame should be used (Eaton *et al.*, 2005). But some elements like vanadium, zirconium, molybdenum and boron has lower sensitivity in the determination by FAAS because the temperature is insufficient to break down compounds of these elements. Samples should be in solution form, or digested to be detected by FAAS. Typical detection limits are around ppm (part per million) range and sample analysis took 10-15 seconds per element. The block diagram of FAAS and GFAAS is depicted in figure 1.

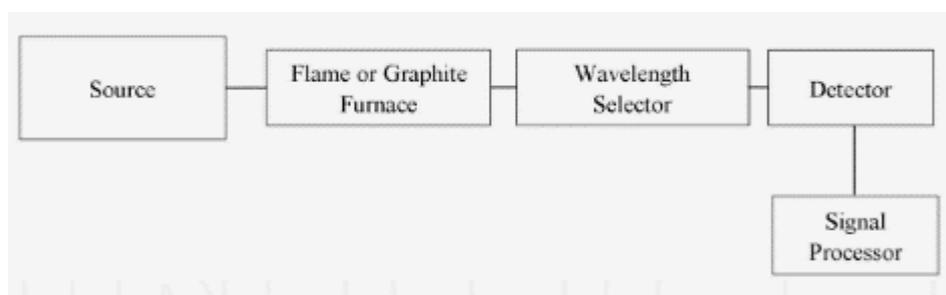


Figure 1. Block Diagram for FAAS and GFAAS (Asli *et al.*, 2013)

Generally, hollow cathode lamps as source, flame or graphite furnace as an atomizer, grating as a wavelength selector and photomultiplier as a detector are used.

Mahmoud *et al.* determined Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb by FAAS after enrichment with chemically modified silica gel N-(1-carboxy-6-hydroxy) benzylidenepropylamine (SiG-CHBPA) (Asli *et al.*, 2013). Afkhami *et al.* determined chromium species based on the catalytic effect of Cr(iii) and/or Cr(vi) on the oxidation of 2-amino-5-methyl-phenol (AMP) with H<sub>2</sub>O<sub>2</sub> by FAAS (Mohamed *et al.*, 2006). Mahmoud *et al.* pre-concentrated Pb(ii) by newly modified three alumina-physically loaded-dithi-zone

adsorbents then determined by FAAS (Mahmoud *et al.*, 2010). Cassella *et al.* prepared a minicolumn packed with a styrene-divinylbenzene resin functionalized with (S)-2-[hydroxy-bis-(4-vinyl-Phenyl)-methyl]-pyrrolidine-1-carboxylic acid ethyl ester to determine Cu in water samples (Cassella *et al.*, 2005). Carletto *et al.* used 8-hydroxyquinoline-chitosan chelating resin in an automated on-line preconcentration system for determination of Zn(ii) by FAAS (Carletto *et al.*, 2008). Gunduz *et al.* preconcentrated Cu and Cd using TiO<sub>2</sub> core-Au shell nanoparticles modified with 11-mercaptopundecanoic acid and analysed their slurry (Gunduz *et al.*, 2011).

ETAAS is basically same as FAAS; the only difference is flame is replaced by graphite tube which can be heated up to 3000°C for atomization. Since sample is atomized in a much smaller volume the atoms density will be higher, its detection limit is much more than FAAS, around ppb (part per billion) range. Graphite furnace program typically consists of four stages; drying for evaporation of solvent; pyrolysis for removal of matrix constituents; atomization for generation of free gaseous atoms of the analyte; cleaning for removal of residuals in high temperature. Generally samples are liquids, but there are some commercial solid sampling instruments also. Analysis took 3-4 minutes per element. 50 and more elements can be analysed by GFAAS (Skoog *et al.*, 1998).

Burguera *et al.* determined beryllium in natural and waste waters using on-line flow-injection preconcentration by precipitation dissolution for electrothermal atomic absorption spectrometry. They used a precipitation method quantitatively with NH<sub>4</sub>OH-NH<sub>4</sub>Cl and collected in a knotted tube of Tygon without using a filter then the precipitate was dissolved with nitric acid injected to graphite furnace (Burguera *et al.*, 2000). Baysal *et al.* accomplished to preconcentrate Pb by cobalt/pyrrolidine dithiocarbamate complex (Co(PDC)<sub>2</sub>). For this purpose, at first, lead was coprecipitated with cobalt/pyrrolidine dithiocarbamate complex formed using ammonium pyrrolidine dithiocarbamate (APDC) as a

chelating agent and cobalt as a carrier element. The supernatant was then separated and the slurry of the precipitate prepared in Triton x-100 was directly analyzed (Baysal *et al.* 2008).

Hydride generation atomic absorption spectrometry is a technique for some metalloid elements such as arsenic, antimony, selenium as well as tin, bismuth and lead which are introduced to instrument in gas phase. Hydride is generated mostly by adding sodium borohydride to the sample in acidic media in a generator chamber. The volatile hydride of the analyte generated is transferred to the atomizer by inert gas where it is atomized. The oxidation state of the metalloid is very important so before introducing to the hydride system, specific metalloid oxidation state should be produced. This method lowers limit of detection (LOD) 10-100 times (Skoog *et al.*, 1998 and Dedina and Tsalev, 1995).

Coelho *et al.* presented a simple procedure was developed for the direct determination of As(ii) and As(v) in water samples by flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS), without pre-reduction of As(v) (Burguera *et al.*, 2000). Cabon and Madec determined antimony in sea water sample by continuous flow injection hydride generation atomic absorption spectrometry. After continuous flow injection hydride generation and collection onto a graphite tube coated with with indium, antimony was determined by graphite furnace atomic absorption spectrometry (Cabon and Madec *et al.*, 2004). Yersel *et al.* developed a separation method with a synthetic zeolite (mordenite) was developed in order to eliminate the gas phase interference of Sb(iii) on As(iii) during quartz furnace hydride generation atomic absorption spectrometric determination (Yersel *et al.*, 2005). Anthemidis *et al.* determined arsenic(iii) and total arsenic in water by using an on-line sequential insertion system and hydride generation atomic absorption spectrometry (Erdogan *et al.*, 2011). Erdogan *et al.* determined inorganic arsenic species by hydride generation atomic absorption spectrometry in water samples after preconcentration/separation on nano  $ZrO_2/B_2O_3$  by solid phase extraction (Erdogan *et al.*, 2011). Korkmaz *et al.* developed a novel

silica trap for lead determination by hydride generation atomic absorption spectrometry. The device consists of a 7.0cm silica tubing which is externally heated to a desired temperature. The lead hydride vapour is generated by a conventional hydride-generation flow system. The trap is placed between the gas-liquid separator and silica T-tube; the device traps analyte species at 500°C and releases them when heated further to 750°C. The presence of hydrogen gas is required for revolatization; O<sub>2</sub> gas must also be present (Karadeniz *et al.*, 2002).

Cold vapour atomization technique is used for the determination of mercury which is the only element to have enough vapour pressure at room temperature. Method is based on converting mercury into Hg<sup>+2</sup>, followed by reduction of Hg<sup>+2</sup> with tin(II)chloride or borohydride. Then produced elemental mercury swept into a long-pass absorption tube along with an inert gas. Absorbance of this gas at 253.7nm determines the concentration. Detection limit is around ppb range. Beside to inorganic mercury compounds, organic mercury compounds are problematic as they cannot be reduced to the element by sodium tetrahydroborate, and particularly not by stannous chloride. So it is advised to apply an appropriate digestion method prior to the actual determination (Skoog *et al.*, 1998).

Kagaya *et al.* managed to determine organic mercury, including methylmercury and phenyl-mercury, as well as inorganic mercury by cold vapor atomic absorption spectrometry (CVAAS) by adding sodium hypochloride solution (Kagaya *et al.*, 2004). Pourreza and Ghanemi developed a novel solid phase extraction for the determination of mercury. The Hg(II) ions were retained on a mini-column packed with agar powder modified with 2-mercaptobenzimidazole. The retained Hg(II) ions were eluted and analysed by CV-AAS (Pourreza and Ghanemi, 2009). Sahan and Sahin developed for on-line solid phase preconcentration and cold vapour atomic absorption spectrometric determination of Cd(II) in aqueous samples. Lewatit Monoplus TP207 iminodiacetate chelating resin was used for the separation and preconcentration of Cd(II) ions at pH 4.0 (Sahan and Sahin, 2012).

However, qualitative analysis cannot be made by AAS because a specific hollow cathode lamp (HCL) is used for each element. Therefore, elements should be determined one by one which make a qualitative analysis almost impossible. In addition, non-metals cannot be determined because their atomic absorption wavelengths are in far UV range which is not suitable for analysis due to absorption of air components (Asli *et al.*, 2013).

Since 2004, new generation high resolution continuum source atomic absorption spectrometer (HR-CS-AAS) which is equipped with high intensity xenon short-arc lamp, high resolution double monochromator, CCD detector are produced. The continuous source lamp emits radiation of intensity at least an order of magnitude above that of a typical hollow cathode lamp (HCL) over the entire wavelength range from 190 nm to 900 nm. With these instruments, aside from the analysis line, the spectral environment is also recorded simultaneously, which shows noises and interferences effecting analysis. Improved simultaneous background correction and capabilities to correct spectral interferences, increase the accuracy of analytical results. With high resolution detector, interferences are minimized through optimum line separation. With these instruments, not only metals and non-metals e.g. F, Cl, Br, I, S, P can be determined by their hyperfine structured diatomic molecular absorbances. There are various papers for fluoride determination by GaF (Gleisher *et al.*, 2010), SrF (Ozbek and Akman, 2012), AlF (Ozbek and Akman, 2012), CaF (Mores *et al.*, 2011), chloride by AlCl (Heitmann *et al.*, 2006), InCl (Huang *et al.*, 2006), bromide by AlBr (Huang *et al.*, 2008), CaBr (Limburg and Einax, 2012), sulfur by CS (Baysal and Akman, 2011), phosphorus by PO (de Campos *et al.*, 2011).

## **2.5 Flame Atomic Absorption Spectrometry (FAAS)**

Flame atomic absorption spectrometry is a quantitative analytical method based on measuring the light absorption of free, ground state atoms. The ground state atoms are excited by electromagnetic radiation (light), while absorbing photons having equivalent wavelength

with the excitation energy. The absorption spectrum of atoms (similarly to emission spectrum) is line spectrum. The lines are present at exactly determined wavelengths and they have a very small, approximately 0,001 nm FWHM (full width at half maximum). This type of absorption spectrum of atoms gives the high selectivity of atomic absorption spectrometry. At the best line of a given element the probability of absorption of other elements is very low thus complex systems containing several elements can be analyzed without the separation of elements. This procedure has great advantage to molecule absorption spectrometry methods where there is a higher probability of optical interfering effect due to the band absorption and usually the analysis of complex systems is possible only after the application of separation techniques. With atomic absorption we measure the concentration of free atoms in the atomizing unit. The relationship between the decrease of light intensity at the wavelength of the examined metal and the concentration of free atoms in a unit of volume is described by Lambert-Beer law as follows:

$$A = \text{Log} \frac{I_0}{I} = a \cdot c \cdot l$$

Where A = Absorbance

$I_0$  = Initial light intensity before absorption

I = Light intensity after absorption

a = Absorption coefficient (Constant depending on material properties)

c = Number of free ground state atoms in the atomizing unit (flame)

l = Length of way passing the light in the atomizing unit.

Thus the absorbance is directly proportional to the number of free, ground state atoms in a unit of volume. Furthermore the number of free atoms in the flame is proportional to the concentration of analyte in the solution. When the concentration is doubled, the number of ground state atoms in the atomization unit is doubled as well. (Of course only when the parameters of analysis of sample and calibrating solutions are the same.)

In order to perform atomic absorption measurements the light of the light source producing characteristic, sharp spectrum of the element to be measured should be led through the flame where the aerosol is present in form of fine spray. The narrow range of the spectrum containing the resonance line of the element is separated from the other part of spectrum with a monochromator. The selected resonance line gets to the light sensing detector (like photomultiplier), of which signal is amplified. To exclude the emitted light of the flame, the light of the light source is chopped with a chopper and in the detector it gives alternating current, while the background radiation of the flame gives direct current. Based on the implementation of it, there are single beam (Figure 2. a and b.) and double beam photometers (Figure 2 c).

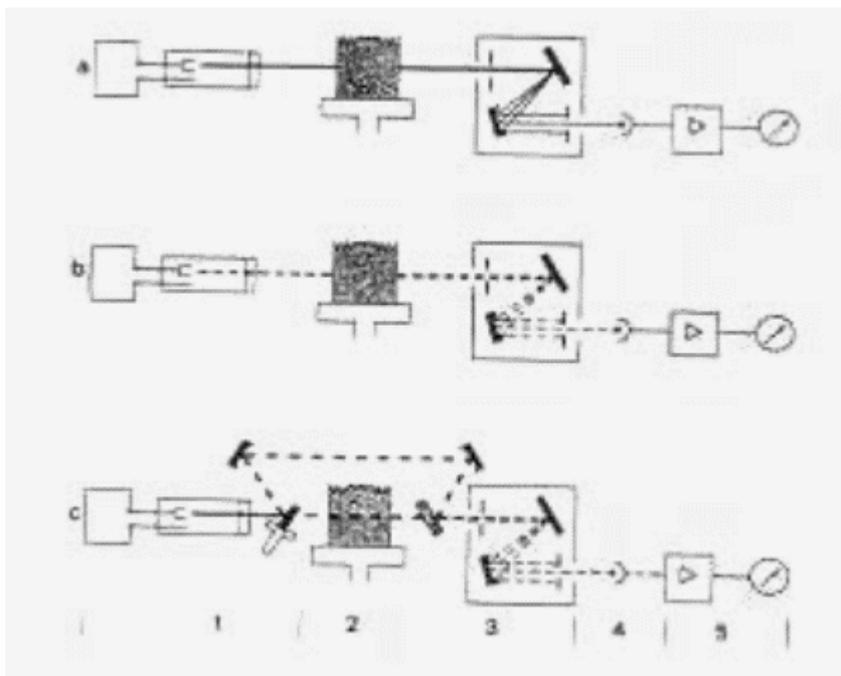


Figure 2. Arrangement of single beam (a, b) and double beam (c) atomic absorption spectrophotometers (1 light source; 2 flame; 3 monochromator; 4 detector; 5 signal processing and displaying unit).

For atomic absorption measurements light sources providing intensive line spectrum are needed and the FWHM of the emitted lines should be small. The hollow cathode lamp (HCL) is such a light source which is a special discharge tube (Figure 3). The cathode is

made from the material of the examined element and it has a cylindrical shape. The discharge is established due to the 300- 400 V potential put between the cathode and anode resulting the electron emission of the cathode. Accelerating the electrons in the electric field gives rise to the avalanche-like ionization of the filling gas of the HCL. Noble gas ions travelling at high speed impact to the cathode and metal atoms are torn out from the surface of the cathode (cathode atomization). The free atoms of the examined elements are produced by this way. These atoms collide with the noble gas ions travelling at high speed and a line spectrum characteristic to the desired element is emitted. HCLs are usually monoelements thus lamps are need to be changed when turning to the measurement of a new element.

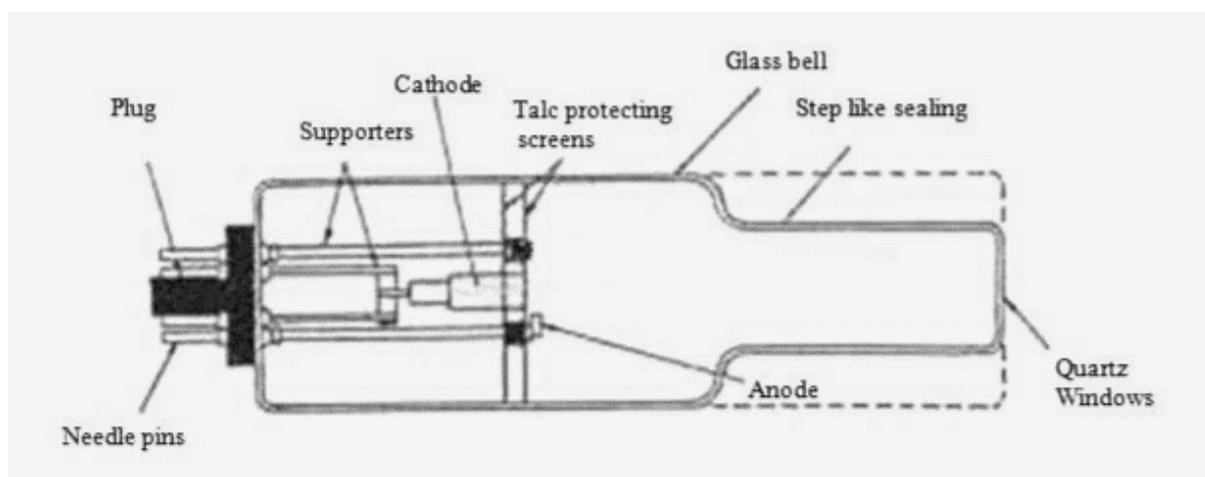


Figure 3. Parts of hollow cathode lamp.

Each elements those have resonance line in that range of the spectrum which can be measured by the detector can be determined with AAS. Most of the instruments can be used in UV and visible range (190-800 nm). Noble gases, halogens and C, H, S, O, N, P cannot be determined since the resonance line of these elements are under 190 nm. The elements of which oxides do not decomposes in flame or which produce oxides or hydroxides in flame can be determined difficultly.

## 2.6 Evaluation Methods

In flame spectrometry comprehensive calibration and standard addition calibration are the two most often used evaluation techniques.

*Comprehensive technique* can be applied in case of big number samples of the same type. The comprehensive solution series (standards) contain increasing quantity of the examined elements. Moreover the standards may contain other components present in the samples (cations, anions, organic compounds, solvents) in average concentration. Since the composition of validation series made by this way is about the same with sample composition, the arising interfering effects will be about the same. The parts of the calibration series are usually diluted from a stock solution with exactly known concentration.

This method provides analytically reliable results only in case of samples belonging to the same type with relatively steady composition. We would determine for example calcium with large error if we used the same composition calcium standard for the analysis of blood serum, water sample and ore solution made from rock pieces. In the mentioned samples not only the concentration of components present besides calcium differ significantly but also the type of arising interfering effects may be different. A typical calibration diagram from comprehensive evaluation method is seen in Figure 4.

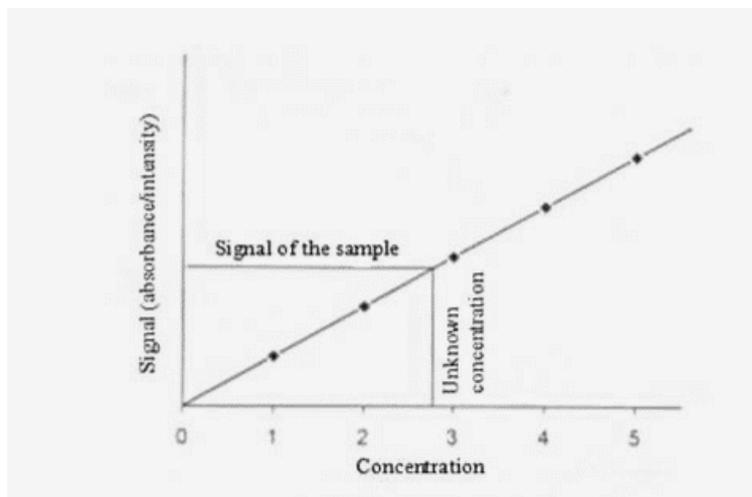


Figure 4. Comparison evaluation method

*Standard addition method* is applied primarily in case of so called exponential interfering effects, when we do not know the cause of interfering effect or we do not know the quality and concentration of interfering components respectively. The point of the method is that the samples are divided into 3-5 equal parts. We give to each portion increasing amount of examined metal ion in the same volume. To the first portion we do not add any metal ion solution thus it contains the examined metal ion in the original concentration (this unknown is the “+0” member in addition series.), to the other members known increasing amount of examined metal solution is given. The results should be plotted like in Figure 5. The linear line fit to measure points (intensity of emission or absorbance) intersects the abscissa axis beyond

0 in negative range. The scale is the same than in positive range. The absolute value of the distance between the intersect and the origin gives the metal ion concentration of the sample.

The condition of the applicability of the method is that a linear line should be able to fit on measure points. To perform standard addition on several samples however makes it much work demanding thus it is not capable for serial analysis. It makes hard to use this method when the volume of sample solution is limited (1-2 mL). In case of complex samples containing mostly organic substance matrixes, standard addition method is often used.

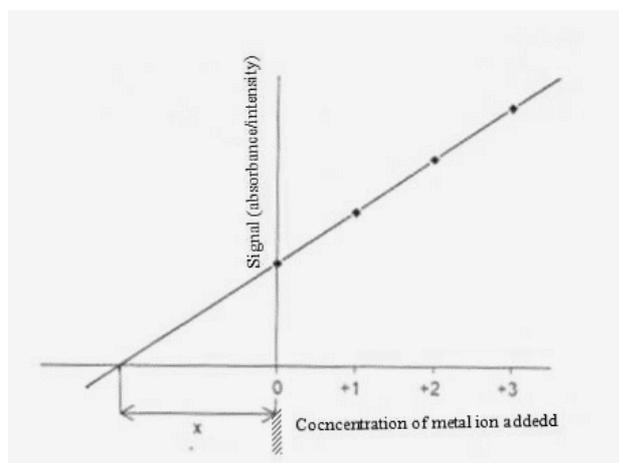


Figure 5. Standard addition method

## 2.7 Vanadium: Beneficial Effects and Toxicity

Vanadium (V) is widely dispersed in the environment in several ways including the leaching of rocks, the combustion of coal or petroleum products, the contamination from the use of fertilizers, and residual slags from the steel industry. As a result, V has been increasingly released into the soil, water and atmosphere (Ringelband and Helil, 2000).

A previous report (Heinemann *et al.*, 2000) showed that patients who had used albumin solutions containing high levels of V could suffer renal damage, especially those patients with existing impaired renal function. Some people in communities in northeastern Thailand are known to suffer health problems with regard to distal renal tubular acidosis. This was thought to have arisen from high environmental levels of V in the soil as higher V levels were also found in these patients urine (Tosukhowong *et al.*, 1999).

Vanadium is a metallic element commonly found in foods, water, soil, air and in the human body. Like some other toxic heavy metals, trace amounts of vanadium are thought to be essential for human health. Some experts believe that this mineral is helping the body's metabolism, while also promoting strong bones and teeth, fertility, proper thyroid function and the production of certain hormones. In industry, vanadium is used as an ingredient in making steel, ceramics and glass. Vanadium finds its way into the body mainly through food and water but also through breathing. However, only about 5-10% of this mineral is actually absorbed in the body where excess vanadium accumulates and may reach toxic levels. High levels of protein, vitamin C, iron, aluminium and chloride in the diet are believed to prevent vanadium from being absorbed in the body. Unabsorbed vanadium is normally excreted through faeces.

All vanadium compounds are considered to be toxic, though they are not regarded as serious health hazard. Adverse health effects of toxic amounts of vanadium can range from loss of appetite and common digestion problems (e.g. nausea, vomiting, stomach pain, gas, diarrhea and loose stool) to damage of the liver and nervous system, kidney failure and lack of growth. Other symptoms of vanadium toxicity include irritation of mucous membranes and the upper respiratory tract, inflammation of stomach and intestines, skin rash, nose bleeding and internal bleeding, dizziness and headaches, cardiovascular problems and behavioural changes.

V contamination from basic slag fertilizers was observed to have toxic effects on cattle after feeding on contaminated fresh hay (Frank *et al.*, 1996). The effect of V on plant growth has also been reported in soybean. It was found that if the concentration of V added to the fluvo-aquic soil exceeded 30mg/kg soil, significantly decreased yields of shoots and roots were obtained. Also, seedling leaves were yellow and withered (Wang *et al.*, 1999). The most toxic oxidation state of V is +5 (vanadate). There is a wealth of evidence that vanadate is absorbed by plant tissues (Bowman, 1983; Ullrich-Eberius *et al.*, 1989) and can inhibit the plasma membrane hydrogen (H<sup>+</sup>) – translocation ATPase (Vara and Serrano, 1982), which is known to play an important role in nutrient element uptake by plant cells.

Vachirapatama *et al.* (2002) revealed that some phosphate fertilizers were contaminated with high concentrations of V (90-180mg/kg). this may suggest that the use of this phosphate fertilizers may cause the V to become widely spread in soils, water and vegetables and it has potential effects to human and animal health (Narumol *et al.*, 2011).

## **2.8 Titanium: Beneficial Effects and Toxicity**

Titanium has significant biological effects on plants, being beneficial at low and toxic at higher concentrations (Kuzel, 2003).

Botanists noticed as far back as the 1930s that in low doses, titanium beneficially affects plant metabolism, stimulating “chlorophyll content, enzyme activities and uptake of major and minor nutrients.” One group of scientists attributes the boost to the hormesis effect, in which low doses of an otherwise toxic substance induce favourable biological responses in an organism (Wang, 1999).

In humans, titanium is extremely effective in correcting the disruptions in a person’s biological electrical currents, thereby eliminating any unpleasant and painful symptoms. Titanium itself is non-toxic and not rejected by the body, the medical industry has embraced it for implants such as hip and joint replacements.

Titanium oxide nano particles have been shown to induce emphysema and lung redness in adult mice. Furthermore, exposure of developing lungs to nano particles may lead to chronic irritation and negative effect on lung development increasing the risk of respiratory disorders. Titanium dioxide has a toxic effect on glial cells in the brain, this may cause brain injury. Titanium dioxide is carcinogenic to humans. Titanium dioxide causes adverse effects by producing oxidative stress, resulting in cell damage, redness, and immune response.

## CHAPTER THREE

### 3.0 MATERIALS AND METHODS

#### 3.1 Materials, Reagents and Instruments

##### 3.1.1 Materials

All chemicals used for this experiment were of analytical reagent grade. Freshly prepared double-distilled water was also used in all experiments.

- Conical flasks
- Volumetric flasks
- Funnels
- Stirring rods
- Oven
- Whatman filter paper
- 63 $\mu$ m metallic sieve
- Sand bath
- Polythene bags

- Plastic bottles
- Plastic spatula
- Plastic bowl
- Stopper
- Metallic spatula
- Teflon beakers
- pH meter
- Pipette
- Stop watch

### **3.1.2 Reagents**

- Nitric acid ( $\text{HNO}_3$ )
- Hydrofluoric acid (HF)
- Perchloric acid ( $\text{HClO}_4$ )
- Hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ )
- Ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ )
- Sodium acetate ( $\text{CH}_3\text{COONa}$ )
- Distilled water
- Buffer solution

### **3.1.3 Instruments**

- Flame Atomic Absorption Spectrometer (Buck System, Model 210 VGP, Made in USA)
- Weighing balance (Mettler Toledo, Model – PR 2002, Mdx 2100g)
- Microprocessor pH meter (Hanna Instruments, Model – pH211, Made in Portugal).

## **3.2 Methods**

### **3.2.1 Sampling**

The location for this study was Tony Farms Limited situated in Koton-Karfe Local Government of Kogi State. Samples (aqueous soil sediment extracts and agricultural drainage water) were collected from the drainage path of the farmland at a distance of 100 meter intervals (100 – 500 meters for the soil samples while 200-500 meters for the water samples) into polythene bags and plastic bottles respectively using a plastic spatula and a plastic bowl.

All samples were transported to the chemistry laboratory of Science Laboratory Technology Department, Federal Polytechnic Idah for analysis.

### **3.2.2 Sample Preparation**

Soil samples were oven dried at 50°C, gently disaggregated and homogenized by pounding using a porcelain mortar and pestle which was washed, rinsed with distilled water and dried intermittently between homogenization of soil samples from each of the different distances. After homogenization, the soil samples were sieved using a 63µm metallic sieve which was also washed, rinsed with distilled water and dried intermittently between sieving of soil samples. Afterwards, samples were placed in polythene bags prior to chemical extraction.

Drainage water samples were allowed to stand for 1 hour and the supernatant which was clear and particle free was decanted into properly labelled sterilized plastic bottles prior to elemental analysis.

### **3.2.3 Soil Characterization**

**Soil pH:** The pH of all soil samples was determined prior to chemical extraction using a deionized water suspension of ratio 1:2:5w/v (Strowbel *et al.*, 2005). The procedure is as follows: 5g of prepared soil samples was accurately weighed into a 50ml extraction tube. 12.5ml of deionized water was added to the soil.

The sample was placed on a shaker and agitated at 30rpm for 10 minutes. The sample was left to stand for 10 minutes. A pH meter was calibrated using buffer solution of pH 4 and 7 and used to measure the pH of the samples.

### **3.2.4 Method of Chemical Extraction**

This was done using the sequential extraction method as mentioned by Tessier *et al.*, (1979) scheme.

### **Procedure**

1g of soil sample was placed into a 500ml conical flask and was shaken with 25ml ammonium acetate (1M-pH7) for 15 minutes and allowed to stand at room temperature for 4 hours. The mixture was filtered using a whatman filter paper into a 50ml volumetric flask and then transferred into a properly labelled sterilized plastic bottle to give an exchangeable cation fraction.

The residue was shaken with 15ml sodium acetate (1M-pH 5) for 15 minutes and allowed to stand for 5 hours at room temperature. The mixture was filtered using a whatman filter paper into a 50ml volumetric flask and then transferred into a properly labelled sterilized plastic bottle to give a carbonate bound fraction.

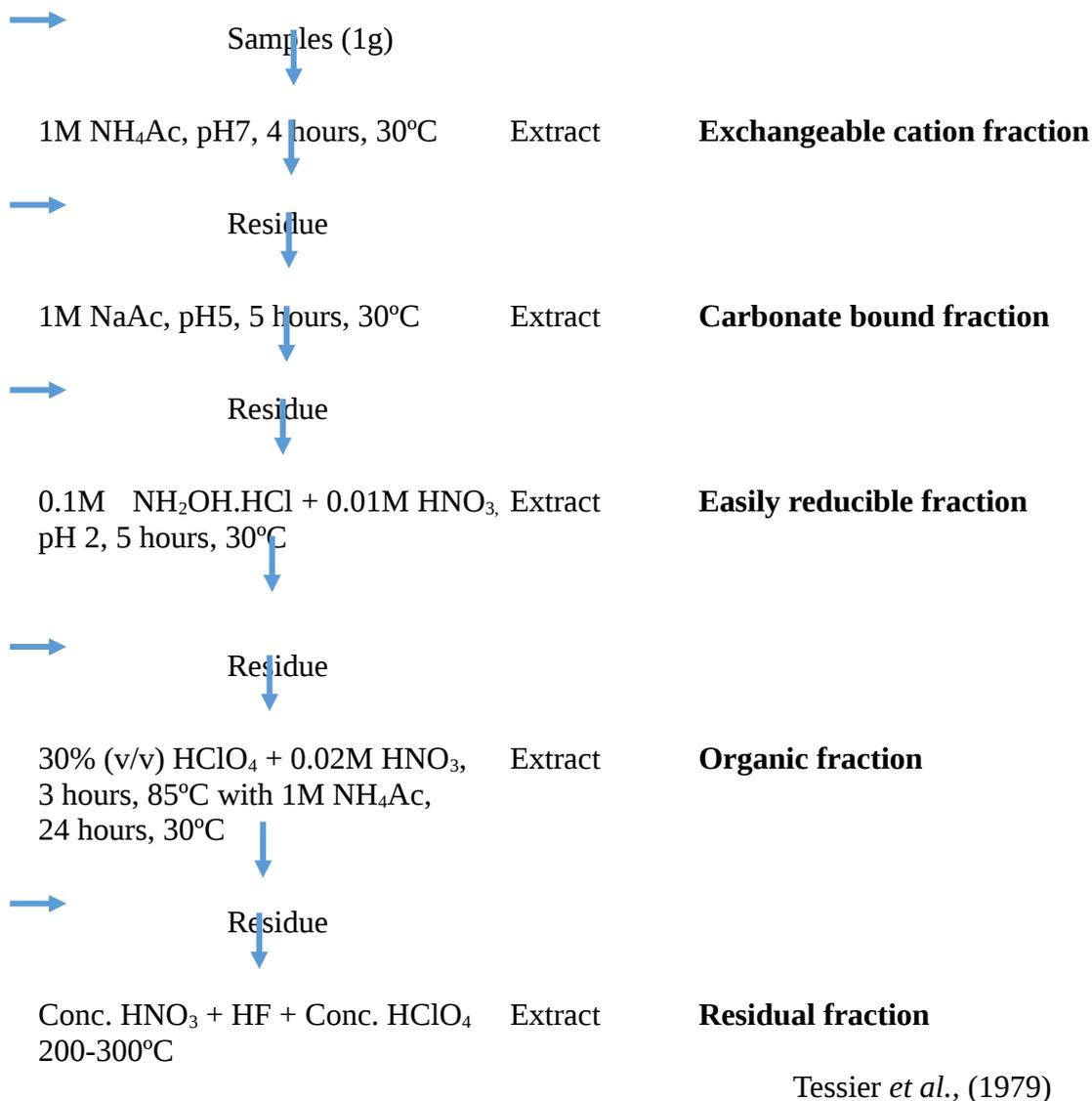
The residue was shaken with 20ml of 0.1M hydroxylamine hydrochloride and 0.01M nitric acid for 15 minutes and allowed to stand at room temperature for 5 hours. The mixture was then filtered using a whatman filter paper into a 50ml volumetric flask and then transferred into a properly labelled sterilized plastic bottle to give an easily reducible fraction.

To the residue, 5ml of 30% perchloric acid and 3ml of 0.02M nitric acid was added and shaken for 15 minutes and allowed to stand at room temperature for 3 hours. The mixture was extracted using 25ml of 1M ammonium acetate for 24 hours at room temperature and filtered into a 50ml volumetric flask and then into a properly labelled sterilized plastic bottle to give an organic fraction.

The residue was placed in a Teflon beaker and 8ml of concentrated  $\text{HNO}_3$  and 4ml of concentrated HF was added to it and allowed to stand at room temperature over night for the initial reaction. Afterwards, 10ml of concentrated  $\text{HClO}_4$  was added to the mixture and the Teflon beaker was tightly stoppered (to reflux the vapours of acid) and heated on a sand bath at a temperature of 200-250°C for 6 hours until complete digestion was achieved which was indicated by a non-turbid solution which was first yellow and then turned white after some minutes. The solution was evaporated to dryness, diluted with distilled water and stirred with a stirring rod. The mixture was then filtered using a whatman filter paper into a 50ml volumetric flask. The filter paper was washed with 10% (v/v)  $\text{HNO}_3$  and the filtrate mixture was transferred into a properly labelled sterilized plastic bottle to give a residual fraction.

All steps in the procedure were repeated for all soil samples from the different distances. Samples were analyzed within 30 days after chemical extraction.

**Figure 6 Extraction Method as Mentioned in Tessier *et al.*, (1979) Scheme**



### 3.3 Method of Analyzing Agricultural Drainage Water Sample

Standard methods for the examination of water and waste water from the United State Environment Protection Agency (USEPA, 1986) were used for the determination of the total

concentration of trace elements such as titanium and vanadium in the agricultural drainage water sample.

The following steps were carried out for the analysis of water: 50g of ammonium acetate solution was dissolved into 60ml of distilled water. 50ml of each water sample was weighed into a beaker and 5ml of concentrated nitric acid was added. The prepared sample was heated on heating mantol until the volume decreased to 20ml.

10ml of perchloric acid was added to each sample and heated to see fumes. After heating, the prepared ammonium acetate was added to the solution to make it up to a mark of 50ml on the calibrated beaker. After adding ammonium acetate it crystallized. Then it was heated again to dissolve. It was poured back to its different container and was taken for analysis using flame atomic absorption spectrometer.

All these elements were analyzed using atomic absorption spectrophotometer. In the process of the analysis, two sets of internal standard were run, one at the beginning and the other in between the analyses to have a check on the accuracy and precision of the results.

**Table 2** Preparation of Standard Solutions

<b>Molecular Formula of (ml) Solutes</b>	<b>Molarity (M)</b>	<b>Molecular Weight (g)</b>	<b>Weight of solute (g)/ volume of Solute (ml)</b>	<b>Volume of solvent</b>
CH <sub>3</sub> COONa	1.00	82.00	82.00g	1000
NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	1.00	77.08	77.08g	1000
NH <sub>2</sub> OH.HCl	0.10	6.95	6.95g	1000
HClO <sub>4</sub>	30% (v/v)	-	30ml	70
HNO <sub>3</sub>	10% (v/v)	-	10ml	90

Conversion from g to ml: mass (g) of  $\text{HNO}_3 \div \text{Density of } \text{HNO}_3 (1.42\text{g/ml}) = \text{ml of } \text{HNO}_3$

$\text{HNO}_3$	0.01	0.63	0.44	1000
$\text{HNO}_3$	0.02	1.26	0.89	1000

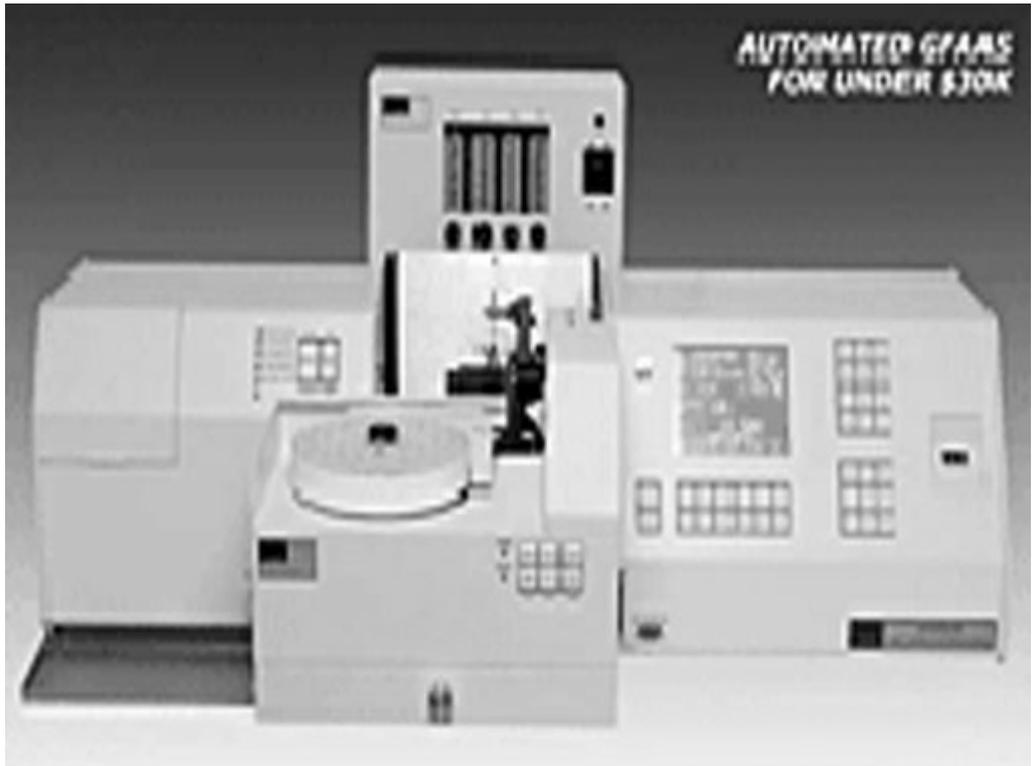
### 3.4 Spectrophotometer Model used for Elemental Analysis

#### Buck Model 210 VGP Atomic Absorption Spectrophotometer

The Buck 210VGP atomic absorption spectrophotometer is designed to measure the concentration of elemental metals in solution. It provides integrated measurements in absorbance or emission intensity, as well as sample concentration in comparison to standard solutions. The readings can be integrated over a period from 0.5 to 10 seconds. For the transient signals obtained using flame-less techniques (cold vapor, hydride, and graphite furnace), absorbance is determined using peak area integration.

The Buck 210VGP can be calibrated using up to 8 concentration values, with units of mg/L, ppm, ppb, mEq/dL, mM/dL, mg/dL and %. Calculations can be performed using linear regression, 2<sup>nd</sup>, 3<sup>rd</sup>, and 4<sup>th</sup> order curves. Optional accessories allow the user to print absorbance data, background absorbance and concentrations in real time, and to collect absorbance values using a laboratory recorder. The Buck 210VGP interfaces with the Analyze software package for sophisticated data processing, documentation and reporting. An external computer is also connected to process the data by using a communications program to download the data into a spreadsheet program.

Figure 7. Buck Model 210VGP Atomic Absorption Spectrophotometer



(Buck scientific, 2003).

Table 3. Buck 210VGP Instrument Specification

<b>Wavelength Range</b>	190 to 900nm, Accuracy $\pm 0.2\text{nm}$ , Precision $\pm 0.1\text{nm}$ .
<b>Monochromator/Optics</b>	250mm Ebert mount, 600 lines/mm grating, 0.2 – 0.7 – 2.0nm band pass.
<b>Hollow Cathode Lamp Supply</b>	Triple HCl power supply; 3 to 75Ma peak in NORMAL mode, 3 to 75mA in GIANT PULSE mode. The 205 has a two lamp design.
<b>Background Correction</b>	Deuterium – in – line (see through) configuration, pulsed illumination, hot cathode, variable frequency, corrects from 190-1900nm.
<b>Burner/Nebulizer</b>	Polypropylene spray chamber with pre-mix burner and high efficiency adjustable nebulizers (SS), Titanium burner heads for

	Air/Acetylene, Argon/Hydrogen and Nitrous Oxide/Acetylene operation.
<b>Microprocessor</b>	Computer control by 80C188 chip, 8/16 bit operation, 12/24 MHz clock speed; non-volatile SRAM storage of > 200 method files.
<b>Integration/Response Range</b>	User selectable times from 0.5 to 10 seconds for continuous (flame) and transient (furnace, hydride) signals.
<b>Calibration</b>	Automatic, weighed least square fit to 1 <sup>st</sup> , 2 <sup>nd</sup> , 3 <sup>rd</sup> , or 4 <sup>th</sup> order functions, up to 8 points.
<b>Display</b>	16-line backlit liquid crystal display for all text and graphics.
<b>Output Modes</b>	LCD display, IEEE-488 parallel port for dot-matrix printer, RS-322 serial port.
<b>Dimensions/Weight</b>	39" Lx11"W x 12"H; 50lbs (81 lbs shipping weight).
<b>Power supply</b>	100-240 VAC operating range, 50/60 Hz AC, <150 watts.

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Buck Scientific, 2003)

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION

#### 4.1 Results

The result of the determination of the pH and concentrations of Titanium (Ti) and Vanadium (V) from agricultural drainage water and aqueous soil sediment extracts in Tony

farms limited Koton-Karfe Local Government Area, Kogi state by atomic absorption spectrometer after five-stage sequential extraction procedure are shown in the tables below.

Table 4. pH of Agricultural drainage water samples collected from Koton-Karfe L.G.A, Kogi state, Nigeria.

Distances (m)	pH	Buffer calibration	Temperature
200	4.13	3.73	29.4
300	5.54	3.73	30.8
400	4.84	3.76	30.7
500	5.08	4.18	30.6

Table 5. pH of Aqueous soil sediment extracts collected from Koton-Karfe L.G.A Kogi state, Nigeria.

Distances (m)	pH	Buffer calibration	Temperature
100	4.06	3.75	30.5
200	4.34	4.17	30.6
300	4.53	3.76	30.3
400	4.43	3.69	29.5
500	4.11	3.83	30.1

Table 6. Result for the Sequential extraction procedure for Titanium (Ti)

S/N	Soil sample	Exchangeable Cation fraction	Carbonate bound fraction	Easily reducible fraction μg/g	Organic fraction	Residual fraction	Total
1.	100m	1.90	10.09	1.01	8.14	1.66	22.80
2.	200m	1.50	3.60	2.73	8.20	1.70	17.73
3.	300m	2.08	3.17	1.33	9.53	1.78	17.89

4.	400m	1.28	2.32	7.84	10.56	1.68	23.68
5.	500m	1.45	3.57	2.31	4.78	5.17	17.31
6.	Mean	1.65	4.55	3.04	8.24	2.40	19.88

Table 7. Result for the Sequential extraction procedure for Vanadium (V)

S/N	Soil sample	Exchangeable Cation fraction	Carbonate bound fraction	Easily reducible fraction μg/g	Organic fraction	Residual fraction	Total
1.	100m	1.44	8.01	0.89	4.62	1.23	16.19
2.	200m	1.17	2.82	2.58	4.80	1.45	12.82
3.	300m	1.57	2.21	1.13	5.42	1.31	11.64
4.	400m	1.03	1.68	0.88	5.63	0.91	10.13
5.	500m	1.09	4.76	1.80	2.64	2.72	14.19
6.	Mean	1.26	3.90	1.46	4.62	1.52	12.99

Table 8. Result for the analysis of water samples

S/N	Element	200m	300m	400m	500m	Mean
1.	Ti	25.30	25.30	28.90	24.40	25.98
2.	V	24.70	23.90	29.70	22.70	25.25

From Table 6, the exchangeable fraction of Ti occur with a range of 1.28 to 1.90μg/g for the carbonate bound fraction of Ti the observed concentration ranged from 2.32 to 10.09μg/g while for easily reducible fraction of Ti the concentration in the range of 1.01 to 7.84μg/g was observed. The organic fraction component of Ti show the range of 4.78 to 10.56μg/g while the residual fraction indicated the range of 1.66 to 5.17μg/g. The total Ti component in all the fractions of the soil sample range from 17.31 to 23.68μg/g.

For Table 7, which is the speciation of V for soil sediment extracts, the exchangeable fraction ranged from 1.03 to 1.57μg/g while the carbonate bound and easily reducible fractions range from 1.68 to 8.01μg/g and 0.88 to 2.58μg/g respectively. The organic bound and residual fractions of V occurred with a range of 2.64 to 5.63μg/g and 0.91 to 2.12μg/g

respectively. The total V concentration in all the soil samples at different distances range from 10.13 to 16.19 $\mu\text{g/g}$ .

From the results of the analysis of water samples as depicted from Table 8. Ti occurred in the range of 24.40 to 28.90ppm with a mean of 25.98ppm. V occurred in the range of 22.70 to 29.70ppm with an average occurrence of 25.25ppm.

## 4.2 Discussion

From Table 6, Ti had a high concentration at 300m with a value of 2.08 $\mu\text{g/g}$  while at 100m the observed value of Ti is 1.90 $\mu\text{g/g}$ . the variations in the value of Ti in the exchangeable fraction may be ascribed to leaching and run-off (Williams and David, 1976). The carbonate bound fraction of Ti decreased progressively from 100m (10.09 $\mu\text{g/g}$ ) to 400m (2.32 $\mu\text{g/g}$ ) this also could be ascribed to leaching. pH equally played an important fraction in the migration of Ti in the soil. The observed pH (Tables 4 and 5) are all low and therefore the metal solubility increases with low pH (Buyks *et al.*, 2002).

The carbonate bound fraction showed similar trend with that of exchangeable fraction. It was generally observed that the farther the distance from the drainage source, the lower the concentration of the titanium species in both fractions. This may however, be ascribed to chemical speciation along the drainage source.

The easily reducible organic and residual fractions may be attributed to complex formation for the organic fraction. Ti has the tendency to form complexes that are more labile, and are present in humic acid fractions (Senesis *et al.*, 1989).

V speciation in the exchangeable fraction decreases slightly from 100m to 200m with a value of 1.44 $\mu\text{g/g}$  and 1.17 $\mu\text{g/g}$  respectively. This reduction may equally be ascribed to leaching and run-off. At 300m the value of V in the exchangeable fraction increased to

1.57 $\mu\text{g/g}$  and afterward reduced to 1.03 $\mu\text{g/g}$  at 400m. Thus, 300m sampling point may be ascribed as the zone of transition for V.

The carbonate bound fraction of V indicated a high concentration at 100m with a value of 8.01 $\mu\text{g/g}$ . This, however, decreased progressively to 400m with a value of 1.68 $\mu\text{g/g}$ . This variation may be attributed to redox processes as a result of the manifestation of different oxidation states of V in the environment (Motelica-Heino *et al.*, 2003).

The V observed in the easily reducible fraction are quite low at the 100m with a value of 0.89 $\mu\text{g/g}$  in comparison to the carbonate bound and exchangeable fractions. This low value in the easily reducible fraction may be due to chemical speciation of V species. V may occur in +2, +3, +4, and +5 oxidation states, from which V(+4) and V(+5) are the dominant and more soluble species moderately reducing and aerobic conditions. Reduction of V(+4) decreases V mobility (Fox and Doner, 2002).

The implication of the high exchangeable and carbonate fractions of both Ti and V is that this fractions are the lethal dose and can easily bio-sorb into the plant matrix and therefore leads to bio-accumulation in the plant tissues.

The variations in the organic and residual fractions for both Ti and V may principally be due to variations in the pH along the trajectory of the water course as indicated in Table 4 and 5

Results for Ti and V analysis in the water samples showed exceedingly very high concentrations. This high concentration values of Ti and V may be principally be due to leaching and run-off, pH and complex formation.

## **CHAPTER FIVE**

### **5.0 CONCLUSION AND RECOMMENDATION**

## **5.1 Conclusion**

From the analysis of the results above, it was observed that reasonably large quantities of Ti and V are available for bio-sorption in the sediment samples. This is evident in the water analysis where the mean values of Ti and V are 25.98ppm and 25.25ppm respectively. It is therefore, inferred that bio-accumulation has high chances of occurrence in the agricultural drainage area of Koton-Karfe Local Government of Kogi state.

## **5.2 Recommendation**

It was found that the agricultural drainage water of Tony Farms Limited which is discharged into Enyoji River, a tributary of river Niger is grossly polluted with heavy metals (Ti and V). This informs the need for proper treatment of agricultural waste water prior to its discharge into the environment.

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