ADDIS ABABA UNIVERSTY

DEPARTMENT OF CHEMISTRY

DETERMINATION OF HEAVY METALS IN AKAKI RIVER WASTE WATER BY FLAME ATOMIC ABSORPTION SPECTROSCOPY(FAAS)

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January, 2018

DETERMINATION OF HEAVY METALS IN AKAKI RIVER WASTE WATER AND HOLETA WATER BY FLAME ATOMIC ABSORPTION SPECTROSCOPY(FAAS)

A Graduate Project Submitted to the Department of Chemistry in Partial Fulfillment of Requirements For the Degree of Master of Science in Chemistry

By

Bezabih Aderaw

January, 2018

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Table of Contents

Contents **Page**

List of Tables

List of Tables Page

List of Figures

List of Figures **Page**

List of Abbreviations

BDL	Below Detection Limit
EDWS	Ethiopian Drinking Water Standard
FAAS	Flame Atomic Absorption Spectroscopy
FAO	Food and Agricultural Organization
GDWQI	Global Drinking Water Quality Index
GEMS	Global Environmental Monitoring System
HARC	Holeta Agricultural Research Center
MDL	Method Detection Limit
NEMA	National Environmental Management Authority
SD	Standard Deviation
UK	United Kingdom
WHO	World Health Organization

DETERMINATION OF HEAVY METALS IN AKAKI RIVER WASTE WATER AND HOLETA WATER BY FLAME ATOMIC ABSORPTION SPECTROSCOPY(FAAS).

ABSTRACT

The present project work aimed to study Zn, Ni, Cd and Pb concentrations in Akaki and Holeta rivers.

The water samples were collected from Akaki and Holeta Rivers randomly in two months (October and December) and analyzed for the concentrations of Zn, Ni, Cd and Pb using Flame Atomic Absorption Spectrometry (FAAS). The mean levels of Zn, Ni, Cd and Pb in the studied River water are (5.82±0.32, 0.4801 ± 0.04, 0.0111 ± 0.02 , BDL) mg L^{-1}in Akaki river and (0.82 ± 0.07, BDL, BDL, BDL) in Holeta river respectively.

According to this study the level of Zinc and Nickel obtained in Akaki river were higher than the level set by World Health Organization (WHO) which is alarming to risks to the human health.

CHAPTER ONE

1. Introduction

1.1. Background

Heavy metals are defined as metallic elements that have a relatively high density compared to water (Fergusson, 1990). Most heavy metals are toxic if it is taken higher than the guide lines given , heavy metals also include metalloids, such as arsenic, that are able to induce toxicity at low level of exposure. In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals. Also, human exposure has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic, and technological applications (Bradi, H., 2002).

River water has been and is still being used for many purposes, which include drinking, irrigation, animal farming, recreation and serves as habitat to numerous organisms. The availability of good quality water is an indispensable feature for preventing diseases and improving quality of life (Samara and Binghila et al., 2008).

Heavy metals enter rivers and lakes from the discharge of various treated and untreated liquid wastes to the water bodies (APHA , 2005; Alaa and Osman, 2010).

There are over ten (10) heavy metals that include cobalt (Co), lead (Pb), mercury (Hg), arsenic (As), thallium (Tl), nickel (Ni), manganese (Mn), zinc (Zn), cadmium (Cd) and chromium (Cr) that have a particular significance in ecotoxicology, since they are highly persistent (Storelli ,2005). The levels of metals such as Mn, Zn, Ni are toxic beyond a certain limit, where as Pb, Cr and Cd are toxic even in trace amounts (Bury , 2003; Fernandes ,2008). Toxicity is realized when the levels of these heavy metals are higher than the recommended limit which is different for individual elements in drinking water. The heavy metals Pb, Ni, Mn, Zn, Cd and Cr have the following WHO recommended limits: 0.01 mg/l, 0.07 mg/l, 0.4 mg/l, 3.0 mg/l, 0.003 mg/l and 0.05 mg/l respectively for drinking water (Oguzie and Izevbigie, 2009).

Exposure to high levels of these heavy metals can among many effects severely damage the brain and kidneys, cause miscarriage in pregnant women, damage the organs

responsible for sperm production in men and it may ultimately cause death (Karin and Terry, 2004).

In Addis Ababa, there are 12 river basins, they all are tributaries of the main Akaki river. The tributaries of Akaki river include Kebena, Banche Yekitu, Kortamie, Bulbula, LiquSoramba, Kotebe and Fincha rivers.

Akaki river consists of two main branches, the confluence of which is at Aba Samuel reservoir. The two branches are little Akaki that flows through the western part of the city, rises north west of Addis Ababa on the flanks of wochecha mountain and flows for 40 Km before it reaches the reservoir and the big Akaki river flows through the eastern part of the city which rises from north east part of Addis Ababa (Entoto kidahine mihiret) area flows in to Aba Samuel reservoir after 53 km (Wassie TA 2008).

In Ethiopia, the increasing human population, uncontrolled urbanization, inadequate sanitation and infrastructure cause serious quality degradation of surface water. Nowadays water pollution from disposal of industrial waste water is becoming an environmental concern in Addis Ababa city and its vicinity areas, where most (more than 40%) of large and medium scale manufacturing industries are located along the river banks which are mostly found on the western and southern part of the city and discharge this effluent directly to the Akaki river without any kind of treatments. Thus the rural population living on the fringes of the city are at risk since the Akaki river is a source of drinking water and irrigation area(Mulu A., Ayenew T., Berhe S. 2013).

Heavy metals have the capacity to accumulate in the food web especially in fishes, vegetables, cow's milk (Addisu G. 2009). A number of researches has been conducted in vegetables grown in polluted soil and irrigated by waste water in Addis Ababa and the result shows that the vegetables have a capacity to accumulate large concentration of heavy metals above the recommended maximum limit (Itanna F.,2002, Schwarzenbach RP, Eglit, HofstetterTB, 2010 Mohammed A. 2007).

Ethiopia is endowed with a huge surface and ground water resources. Many perennial and annual rivers exist in the country. Awash basin is one of the 12 basins in Ethiopia. Holeta River is one of the rivers found in the upper part of the Awash basin and facing challenges of runoff

variability and scarcity of water during the dry season. Holeta River is the main source of surface water in the study area; it is a perennial river having three major users and these are Holeta Agricultural Research Center (HARC), Tsedey Farm and Village Farmers. Major crops grown by irrigation are potato, cabbage, barely and apple.

1.2 Statement of the Problem and Justification

Water basins like rivers, ponds especially Akaki river are polluted with toxic heavy metals that come from untreated urban, agricultural and industrial effluents. This may result in bio-accumulation of heavy metals in humans using water directly and eating agricultural products from this river since its tributaries pass through populated residential areas, towns, industrial and agricultural sites. The analysis of heavy metals that include lead, nickel, Zinc, and cadmium is therefore justified to provide precautionary use of the water, as well as provide a basis to aware government authorities such as National Environmental Management Authority (NEMA) towards management of discharge pollutant wastes into the river.

1.3 Objective of the Study

1.3.1 General Objective

To assess the levels of selected toxic heavy metals in Akaki and Holeta river, Ethiopia.

1.3.2 Specific Objectives

I. To determine levels of Pb, Ni, Zn and Cd in Akaki river and to compare with WHO standards.

II. To determine levels of Pb, Ni, Zn and Cd in Holeta river which is used for comparison with Akaki river heavy metal contents.

CHAPTER TWO

2. Review of Literature

2.1. Minerals in the Diet

Varieties of metals found in a range of foods in the diet are termed as minerals. These minerals can be macro minerals, those that are needed by the body in relatively large amounts, e.g. sodium, potassium, calcium, and magnesium. They are present in virtually all cells of the body, maintaining general homeostasis and are required for normal functioning (Kehoe, 1994). Acute imbalances of these minerals can be potentially fatal, although nutrition is rarely the cause of these cases. Diet can affect levels of 12 macronutrients in the body, but effects are generally chronic, e.g. a high intake of sodium can lead to hypertension (FNBIM,1997).Micro/trace minerals are those needed in small amounts, e.g. selenium, iron, zinc, copper, manganese, molybdenum, chromium, arsenic, germanium, lithium, rubidium and tin. Many of these minerals have been classed as essential elements; necessary for utilization by the body to ensure good health, but the function of these minerals and their benefits to the body is still uncertain and has been widely speculated. They contributes to good health if they originate from an organic source because they have essentially been processed. Plants take up minerals from the ground, digest them, making them ionic so that when consumed by humans, assimilation into the body occurs much more easily, and toxicity by accumulation does not occur. However micro minerals from inorganic sources, such as heavy metals, cannot be used by the body as they tend to buildup in the tissues (FNBIM, 1989).

Much research has been carried out concerning the role of minerals in the body, but in many cases, difficulties in investigating their individual effects has been expressed because intake is often in combination with other vitamins and minerals (FNBIM, 2001), e.g. fruit and vegetables contain several minerals. There is, however, strong evidence that supplementation of certain minerals would benefit those suffering from deficiency disorders.

2.2. Heavy Metals

The term Heavy Metals refers to any metallic element that has a relatively high density and is toxic or poisonous at low concentration (Lenntech, 2004). Heavy Metals are a general collective term, which applies to the group of metals and metalloids with atomic density 5 times or more higher than water (Syman and Huton,1986;Nriagu,1988; Hawks,1997).Heavy Metals include Cadmium (Cd), Copper (Cu), Lead (Pb), Zinc (Zn), Mercury (Hg), Arsenic (As), Silver (Ag), Chromium (Cr), Iron (Fe) and Platinum (Pt). Copper and Zinc are essential trace elements for living organisms at low concentration (<10 mg/L) per day. However, they become toxic at high concentration (>10 mg/L). Most of these metal (Cd, Cu, Ni, Hg, As, Ag, Cr and Fe) can be released from the industries are in simple cationic forms (Volesky, 1995).

The characteristics of heavy metals are described by Wang (2006). Toxicity that can last for a long time in nature. Heavy Metals cannot be degraded and are very toxic even at low concentrations (1.0-10.0 mg/L). Heavy Metals are dangerous because they tend to bio-accumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemicals concentration in the environment. Compound accumulate in living things any time they are taken up and stored faster than they are broken down (Metabolized) and excreted (Tsoumbarist et al.,1994).World Health Organization (WHO) has established levels of metals in foods above which they should not be consumed. For this reason the levels of trace metals in our food should be of much importance and concern to us.

2.3. Pollution Problems

Heavy metal pollution comes from the need to immobilize the metals released to the environment or mobilized by and partially lost through human technological activities. It has been established that dissolved metals (particularly heavy metals) escaping into the environment pose a serious health hazard. They accumulate in living tissues throughout the food chain, which has humans at its top, multiplying the danger. Thus, it is necessary to control emissions of heavy metals into the environment. Due to increase in the world population and development of industrial applications, environmental pollution problem has become a series result. Communities produce both liquid and solid wastes.

The liquid -wastewater is essentially in industrial effluent and the water thrown out by community after it has been used in a variety of applications. In recent years, heavy metals, besides other pollutants, have increased to reach dangerous levels for living environment in many regions. The presence of toxic and polluting heavy metals in wastewaters from industrial effluents, water supplies and mine waters and their removal has received much attention in recent years. The amount of heavy metals that industrial wastewaters often contain is considerable and would endanger public health and the environment if discharged without adequate treatment.

Heavy metals are elements such as Cu (Copper), Cd (Cadmium), Ni (Nickel), Pb (Lead), Zn (zinc), Ag (Silver), Cr (Chromium), Hg (Mercury), Fe (Iron), Co (Cobalt) and As (Arsenic) which are usually associated with toxicity and are natural components of the earth's crust. They cannot be degraded or destroyed.

Table 1.Ranking of risks associated with various heavy metals

Relative priority	High	Medium	Low
Environmental risk	Pb, Cd and Hg	Cr, Co, Cu, Ni and Zn	Al and Fe

Heavy metals are natural components of the soil. Most elements are only present in minimal, insignificant eco-toxicological concentrations in undisturbed locations. A few heavy metals are important as trace elements for physiological processes in plants and animals.

Heavy metals contamination of soil is widespread due to metal processing industries, tannery, combustion of wood, coal and mineral oil (Margesin & Schinner 2005). Heavy metals may reach and contaminate plants, vegetables, fruits and canned foods through air, water, and soil during cultivation (Husain , 1995; Ozores , 1997; Geert ., 1989). Inhalation and ingestion of heavy metals may cause various diseases such as anemia, neuropsychological effects, liver diseases, gastrointestinal pathologies, teratogenic implications (Needleman & Bellinger, 1991). Moreover, it is known that the DNA-damaging effects of certain metals in humans can lead to induction of cancer and a decrease of fertility. In addition, heavy metals in soils may adversely affect soil ecology, agricultural production or products and water quality (Wang et al., 2001). ,

Some metals are essential for life, but if an individual's intake exceeds a certain threshold, toxicity may develop. Metals and minerals in food and fodder are of great interest because of their potential effects on human and animal health. Some have no beneficial biological function but exposures or deficiency may be harmful to health. For example, organic mercury compounds are neurotoxins, exposure to lead can be harmful to neurophysiologic development; inorganic arsenic is a human carcinogen and cadmium can affect renal function. While some elements, such as cobalt, iron and copper are essential to health, they may be toxic at high levels of exposure. Exposure to metals can be in a number of ways, including at work in certain industries, from drinking water and eating contaminated foods (Ministry of Agriculture, Fisheries and Food, UK, 1998a,b).

Heavy metal pollution is a rising environmental problem, which requires immediate attention. With current commercial remediation reagents failing to provide the needed requirements as safe and effective metal chelates, the need for new technology is critical. The emissions of sulfur per day, together with dust loaded heavy metals, both discharged from smelter and industries cause many environmental pollution. The annual mean of the global emissions into the atmosphere reach about 150 ton of sulfur and 3.5 ton of dust loaded with heavy metals (Lacatusu , 1999).

The risk to health from certain elements in food can be assessed by comparing estimates of dietary exposures with the Provisional Tolerable Weekly Intakes (PTWIS) and Provisional Maximum Tolerable Daily Intakes (PMTDIs) recommended by the Joint Expert Committee on Food Additives (JECFA) of Food and Agriculture Organization (FAO) and World Health Organization (WHO) programmers on chemical safety (WHO, 1982a,b, 1989a,b, 1993a,b). Extreme accumulation of heavy metals in agricultural soils through wastewater irrigation, may not only result in soil contamination, but also lead to elevated heavy metal uptake by crops, and thus affect food quality and safety. Heavy metal accumulation in soils and plants is of increasing concern because of the potential human health risks. This food chain contamination is one of the important pathways for the entry of these toxic pollutants into the body of the humans. Heavy metal accumulation in plants depends on plant species, and the efficiency different plants in absorbing metals is evaluated by either plant uptake or soil-to plant transfer factors of the metals. Vegetables cultivated in

wastewater-irrigated soils take up heavy metals in large enough quantities to cause potential health risks to the consumers. In order to assess the health risks, it is necessary to identify the potential of a source to introduce risk agents into the environment, estimate the amount of risk agents that come into contact with the human-environment (Khan et al., 2008). Anthropogenic activities mining, ultimate disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates from different industries and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing threat on human beings. However some of the metals for example Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms, while many other metals like Cd, Cr and Pb have no known physiological activity, (Kar , 2007).

As a result, monitoring heavy metals is important for safety assessment of the environment and human health in particular. Regarding this, it was therefore of necessity to determine heavy metals in water, soil and plant.

2.4. Lead as Pollutant

Lead is regarded as highly hazardous for plants, animals and particularly for microorganisms. The main sources of lead pollution in agriculture and plants are lead mines, fuel combustion, sewage sludge applications and farmyard manure. The maximum acceptable concentration for lead in food stuffs is around 1 mg/kg. Long-term exposure to lead can result in a buildup of lead in the body and severe symptoms. These include anemia, pale skin, a decrease handgrip strength, abdominal pain, nausea, vomiting and paralysis of the wrist joint. Prolonged exposure may also result in kidney damage. If the nervous system is affected, usually due to very high exposure, the resulting effects include severe headache, coma, delirium and death. Continued exposure can lead to decreased fertility and/or increased chance of miscarriage or birth defects (Dobrzansk ., 2005).

The exhausts from vehicles are a major source of the environmental contamination by lead. Lead is present in exhaust gases mainly as lead halides and oxides, but incomplete combustion resualts in about 10% of alkyl lead compounds also being present. Other source of lead emissions are copper and nickel smelters, iron and steel production.

Lead exists in the oxidation states Pb^{+2} and Pb^{+4}, with the divalent form being the more stable in most aquatic environments. The speciation of lead compounds in water is complicated and depends upon a number of factors, principally pH, dissolved oxygen and the concentration of other organic and inorganic compounds. The concentration of lead in waters is usually limited by the solubility of $PbCO_3$, and by its adsorption on to particulate matter (Dojlido and Best 1993).

2.5. Cadmium as Pollutant

Cadmium is a toxic metal and can cause serious health problems. Recently attention has been focused on its availability in water, soil, milk, dietary products, medicinal plants, herbal drugs, etc. The most common sources for cadmium in soil and plants are phosphate fertilizers, non-ferrous smelters, lead and zinc mines, and combustion of fossil fuels (Davies, 1990 and Mc Bride, 1995). Critical levels for cadmium in soil are between 3-5 mg/kg. This level, in most cases, it cannot cause toxic or excessive accumulation concentration in plants; the lowest level of the element concentration in plants that can cause crop yield reduction is between 5-30 mg/kg.

The major route of cadmium exposure for the general population is via food. An increase in soil Cadmium content generally results in an increase of plant uptake of Cadmium although some soil and plant factors may influence Cadmium accumulation by plants. Crops grown in Cadmium contaminated areas have been found to contain elevated Cadmium content compared with normal levels. Therefore, human Cadmium exposure via food in contaminated areas can be many times above normal intakes and lead to Cadmium toxicity.

Cadmium is known to be toxic for living organism even if it is present in low levels (Krejpcio, 2001). Cadmium is obtained from the ore minerals Shale rite (ZnS, CdS) and Greenockite (CdS) (Tadesu, 2011).

2.6 Nickel as Pollutant

Nickel with a density of 8.9 g/cm^3 readily forms alloys with iron, aluminum, zinc, molybdenum, and copper and can be dissolved in dilute acids (Reilly, 2002). The most common oxidation state of Ni is +2, but compounds of Ni^{+} and $Ni^{+3}$are well known, and Ni^{+4} has been demonstrated

(Housecraft and Sharpe, 2008). Nickel (II) compounds are known with all common anions, that is, the sulphide, sulphate, carbonate, hydroxide, carboxylates, and halides. In its compounds, Ni has a number of chemical manufacturing uses, such as a catalyst for hydrogenation, as a cathode in many rechargeable batteries, including nickel cadmium, nickel-iron, nickel-hydrogen, and nickel-metal hydride, and used by certain manufacturers in Li-ion batteries (Davis, 2000). About 60% of world production is used in nickel-steels (particularly stainless steel) (Obasohan, 2008).

Nickel toxicity is generally low, but elevated levels have been reported to cause sub-lethal effects (Nussey et al., 2000). Among the known health-related effects of Ni are skin allergies, lung fibrosis, variable degrees of kidney and cardiovascular system poisoning and stimulation of neo plastic transformation. Nickel sulphide fume and dust is believed to be carcinogenic, and various other Ni compounds may be as well (Kasprzak et al., 2003). The toxicity of Ni carbonyls is a function of both the toxicity of the metal as well as the carbonyl's ability to give off highly toxic carbon monoxide gas, that is explosive in air (Nusseyet al., 2000).

The typical concentrations of Ni in unpolluted surface water are given as 0.015 to 0.020 mg/l (Salnikow and Denkhaus, 2002; Awofolu et al., 2005). Studies in river water have indicated various levels of Ni concentrations compared to the recommended limit of 0.07 mg/l Ni in drinking water by WHO (WHO, 2003; Awofolu et al., 2005; Wachira, 2007). Nickel mean levels of 0.03 mg/l from Nairobi River have been recorded (Wachira, 2007). Awofolu et al., (2005) suggested that possible sources of Ni in surface water included anthropogenic activities, combustion of fossil fuels, old battery wastes, components of automobiles, old coins, and many other items containing stainless steel and other Ni alloys.

2.7 Zinc as a Pollutant

Zinc makes up about 75 ppm of the Earth's crust, making it the 24th most abundant element with a density of 7.14 g/cm$^{3.}$ Zn is normally found in association with other base metals such as Cu and Pb in ores and has a low affinity for oxygen and prefers to bond with sulphur and occurs as ores, such as, sphalerite (ZnS), calamite ($ZnCO_3$) and zincates (ZnO). Zn forms alloys

such as brass and bronze and has been used in construction of buildings, roofing and cladding (Emsley, 2001).

Other uses of Zn include making circuit boards, photocopiers, dry cell batteries and its compounds are used in chemical and pharmaceutical industries such as paints, medicines and nutritional supplements (Reilly, 2002).

The toxicity of Zn is as a result of excessive absorption which suppresses copper and iron absorption. While free Zn^{2+} ion in solution is highly toxic to plants, invertebrates, and even fish (FAO/WHO, 2011). zinc salts are intestinal irritants and can cause nausea, and abdominal pain (ATSDR, 2002). Prolonged exposure to high intakes of Zn results in copper deficiency and subsequent anemia (Reilly, 2002). There is also a condition called the zinc shakes or "zinc chills" that can be induced by the inhalation of freshly formed Zn oxide formed during the welding of galvanized materials. It has been reported that zinc is able to damage nerve receptors in the nose, which can cause anosmia and recommended that consumers should stop using zinc-based intranasal cold products and ordered their removal from store shelves (Johnson et al., 2007; Safty et al., 2008).

2.8. Atomic Absorption Spectroscopy

The technique makes use of atomic absorption spectrometry to assess the concentration of an analyte in a sample. It requires a standard with known analyte content to establish the relationship between the measured and the analyte concentrations and relies on Beer Lambert's law (Skoog et al., 2005; Christian, 2005). The sample is converted into atomic vapours by a process known as atomization. The precision and accuracy of this method depends on the atomization step and therefore a good choice of the atomization method is required. The two types of atomizers are continuous and discreet atomizers. In continuous atomizers the sample is fed into the atomizer continuously at a constant rate giving a spectral signal which is constant with time. Atomization methods that are of continuous type are flame, inductively coupled argon plasma and direct current argon plasma. With the discrete atomizers, a measured quantity of a sample is introduced as a liquid or solid. The spectral signal in this case rises to a maximum and then decreases to zero. An electro thermal atomizer is one of the discrete types.

The atoms then absorb radiations of characteristic wavelengths from an external source. The atoms of lead, nickel, zinc, and cadmium absorb radiations of wavelengths of 283.9nm, 232.0 nm, 213.9 nm, and 228.8 nm respectively from an external source which is usually a hollow cathode lamp (Eser et al., 2004).

This technique has been widely employed for elemental analysis in a number of matrices such as soils, water, nuts, wine and wine products (Navinet al., 2000; Tuzen, 2003). Figure 1. shows a schematic diagram for the components of AAS. The two sources of radiation are continuous source which makes use of deuterium and mercury lamps and a hollow lamp which consists of an anode made of either tungsten wire or wink and a hollow cathode made of either the element of interest or its own salt. Flame atomization method consists mainly of a fuel and oxidant. Their temperatures are determined by flow rate and ratio of oxidant and fuel while the electro thermal atomizer is basically made of carbon rods. The free atoms are vaporized from the carbon atomizer into the optical light path to a monochromator which presents a monochromatic radiation to the detector. The radiations from the monochromator are received by detectors which convert them to electrical signals. Some commonly used detectors are photocells and photo multiplier tubes.

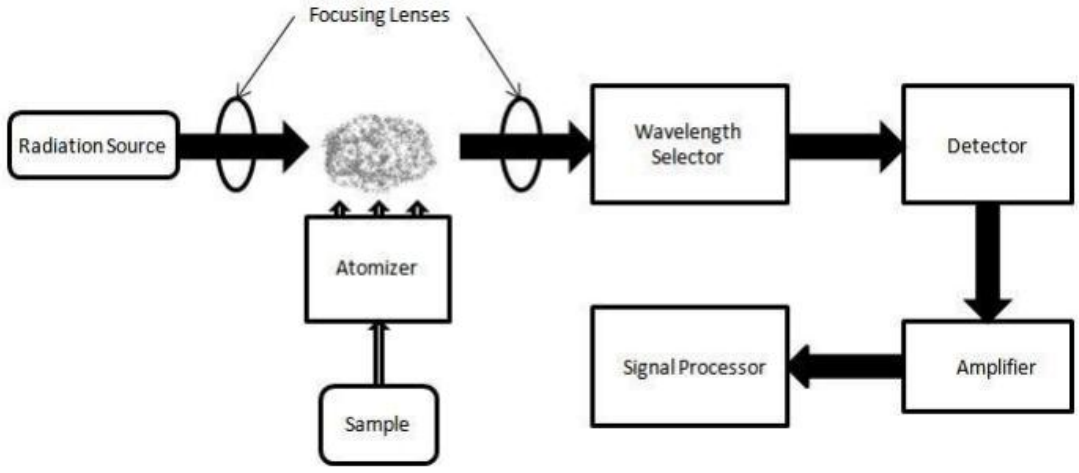


Figure 1*: Schematic diagram of FAAS equipment*

Components of the AAS instrument are :-

a. Radiation source (Hollow cathode lamp)

This is the source of analytical light line for the element of interest and gives a constant and intense beam of that analytical line.

b. Atomizer (Flame)

The atomizer will break complexes to create atoms of the element of interest.

c. Wavelength selector (Monochromator)

A wavelength selector isolates analytical line photons passing through the flame and remove scattered light of the other wavelength from the flame. This only impinges a narrow line on the photomultiplier tube.

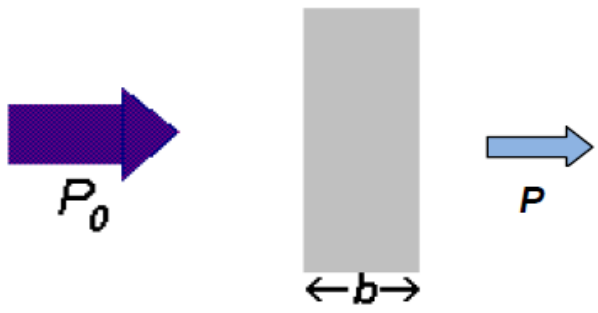
d. Detector (Photomultiplier tube (PMT))

It determines the intensity of the analytical line existing the monochromator. The PMT is the most commonly used detector for AAS.

2.8.1. Beer's low

Many compounds absorb ultraviolet or visible light. When dissolved in water, the absorption of some of the frequency of light causes them to transmit others and the solution are the absorbed color.

The diagram below shows a beam of monochromatic radiation of radiant power P_0, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power P.



The amount of radiation absorbed may be measured in a number of ways:

Transmittance, $T = P / P_0$
% Transmittance, $\%T = 100\ T$

Absorbance,
$A = \log P_0 / P$
$A = \log 1 / T$
$A = \log 100 / \%T$
$A = 2 - \log \%T$

Beer's law - the equation representing the law is straightforward:
A= εbc
Where, A is absorbance (since $A = log\ P_0 / P$).

ε is the molar absorptive with unit of (M^{-1} cm^{-1}).

b is the path length of the sample (cm).

c is the concentration of the compound in solution, expressed in (M).

2.9. Digestion of the Sample

Sample (matrix) digestion plays a central role in almost all analytical process, but is not often recognized as an important step in analytical chemistry, with primary attention being directed to the determination step. This sense of priorities is reflected in the equipment and investment planning of many analytical laboratories. However a welcome trend in recent years points toward fuller recognition of the true importance of sample digestion (decomposition, dissolution) in the quest for high quality analytical result and valid conclusions (Henryc Matusiewicz; 2003).

There are many digestion processes, Some of them are Dry ashing method, wet digestion method, etc.

2.9.1. Dry Ashing Sample

The objective of Dry ashing is to combust all of the organic material till a white ash is detained and to prepare the sample for subsequent treatment using Wet ashing or fusion techniques. This procedure involves heating a sample in an open dish or crucible in air, usually in muffle furnace to control the temperature and flow of air(Argonne, 1992).

Microwave techniques are also available for Dry ashing sample. Dry ashing of the sample is used to determine ash weight as well as non volatile constituents.

Dry ashing methods are comparatively simpler and safer than wet digestion method but may introduce errors due to volatilization(Ali, Zoltai, and Radford 1988).

2.9.2. Wet Digestion Method

Wet digestion methods involve the use of both heat and mineral acid/s. Acids that have been used include H_2SO_4, HNO_3 and $HClO_4$, either in combination or alone (Maria, 2002). Hydrogen peroxide is also used to enhance the reaction speed and to ensure complete digestion. Most laboratories have eliminated the use of $HClO_4$ due to risk of explosion. Wet digestion can be carried out in open vessels, in tubes, on a hot plate or in an aluminum heating block or in closed vessels at elevated pressure (digestion bombs) with thermal or microwave heating. Microwave-assisted digestion is an attractive method, especially for small samples. The applicability of this technique strictly depends on the type of food: carbohydrates are easily mineralized with nitric acid at 180 ^{0}C, while fats, proteins and amino acids cause incomplete digestion due to the relatively low oxidation potential of nitric acid at 200 ^{0}C; these materials require the addition of sulfuric and/or perchloric acid with all the problems related to their use at high temperature and pressure. The type of acid/s used can have important consequences in the measurement step. It is commonly known that in all Atomic absorption spectrometric techniques nitric acid is the most desirable reagent. In spite of occasionally observed signal suppression in its presence, no severe analytical problems are encountered in practice with nitric acid at concentrations up to 10%, sometimes higher, in all Atomic absorption spectrometric techniques as long as its concentration is similar in calibration and sample solutions. Hydrogen peroxide added in most mineralization procedures is also rarely responsible for analytical problems (Arruda, 2007).

Main features associated with wet digestion methods are: (1) much lower temperatures as compared to dry ashing procedures, however minimizing volatilization losses or retentions caused by reactions between analyte and vessel materials, they may lead to incomplete solubilisation of sample constituents and (2) co-precipitation of analyte with precipitates formed by main matrix elements within reactive mixtures.

Wet digestion method was chosen based on its less contamination, lower rate of evaporation, cost and time and extraction efficiency(oliva, raitio, and mingorance 2003).

CHAPTER THREE

3. Material and Methods

3.1. Description of the Study Area

The sample for this study was collected from Addis Ababa city, at the foot of Mount Entoto which is 2300m (7500ft) high above sea level. This city located 9˚ 1' 48" N latitude and 30˚ 44' 24" longitude forms part of the watershed for Awash river. Holeta city, another sampling area, is located in the Oromia zone, surrounding Fininne specifically 9˚ 3' N latitude and 38˚ 30' E longitude and 2391m high above sea level. The selection of study area was based on availability of highly dense factory effluents, peoples waste dumping site, sampling cost, proximity of the study area and largely used for irrigation.

Figure 2. ***Akaki river during irrigation***

Figure 3. Students at irrigation site of Akaki river

3.2. Apparatus and Instruments

The following apparatus and instruments were used in the project work. Poly ethylene bottles, micro pipettes, vial, volumetric flasks, beakers, pipettes, different size measuring cylinders, funnels, graduating cylinders, thermometers, Whatman filter papers no.42, refrigerators, hot plates, Flame Atomic Absorption Spectrophotometer (Analitikjena, Model ZEENIT, 700P, Germany).

3.3.Chemicals

All chemicals were used during analysis are high purity analytical grade reagents; HNO_3 (69 % LR, Breck land scientific supplies, UK), H_2O_2 (30 %) used for digestion of sample and blank. Certified reference material Cd, Zn, Pb, and Ni used for preparation of standard samples were

obtained from Europe accredited lab. Tap water, distilled water, deionized water were taken for washing, rinsing, and preparation of sample.

3.4 Sample Collection

Five water samples were collected from different areas of Akaki river in polyethylene plastic bottles in two consecutive months of dry season. The plastic bottles were washed with soap and tap water then rinsed with distilled and deionized water followed by 0.02 M HNO_3 to maintain constant pH of the sample. The same amount of samples were taken from Holeta River with the same material. The samples from each river were homogenized in one plastic bottle to get a representative sample. Then the samples were sealed, transported to the laboratory and stored in a refrigerator for digestion.

3.5 Digestion of River Water

50 ml of acidified sample was measured and put in clean 20% nitric acid soaked conical flask and 5 ml of analytical grade nitric acid was added. The mixture was heated at 95 ℃ with addition of 3 ml H_2O_2 until there were no brown fumes and the volume reduced to 10 cm^3 for one hour on a hot plate. The mixture was then filtered using Whatman filter paper no.42 in 50 ml volumetric flask dilate to the label mark with deionized water. The samples of water were digested in triplicate then labeled and stored for awaiting analysis. For background correction three blanks were digested as pre-test samples and each analyzed for the required metal by FAAS.

3.6 AAS Operating Conditions

The equipment used in this study include hot plate and Atomic Absorption Spectrophotometer. The operating condition for the AAS are given in table below.

Table 2. The AAS operating conditions

Operating parameters	Pb	Ni	Zn	Cd
Wavelength (nm)	283.3	232	213.9	228.8
Slit width (nm)	1.2	0.2	0.5	1.2
Flame type	Air Acetylene			
Photo multiplier tube (PMT)	262	375	461	252
Lamp current (mA)	2	3	2	2
Detection limit (ppm)	0.03	0.07	0.012	0.012

3.7 Stock Solution, Working Standards and Calibration of the Instrument

In the metal analysis procedure, the standard containing stock solution (1000 ppm) was obtained from Europe accredited lab. That is, the stocks used to prepare the intermediate standards and working standards are Certified Reference Material (CRM).The intermediate standards and working standards are prepared from the stock solution by serial dilution with deionized water. After the working standards are prepared the instrument was calibrated to obtain good correlation between absorbance and concentration which is used to determine the unknown concentration of the sample.

3.8 Method Detection Limit

Method detection limit (MDL) is defined as the minimum concentration of analyte that can be measured and reported with 99% confidence level. But it may not necessarily be quantified as an exact value (Harries, 1982). Method detection limit was calculated by multiplying the standard deviation of the blank by three.

3.9 Recovery Test

Matrix Spiking is a technique that is used to evaluate the performance of an analytical procedure when testing a specific sample (matrix) type. In other words, a matrix spike test helps answer the question “Are we getting good (valid) results when we use this method to test this sample or this

type of sample?". A "good" matrix spike result increases our confidence in the accuracy and validity of the sample test results.

A Matrix Spike (MS) is generated by adding a known amount (a spike) of analyte to a sample, testing the spiked sample, and determining weather we have recovered the amount that we added or not.

In practice, two portions of the sample are prepared for testing. In the "matrix spike" portion, a known amount of standard is added (to increase the concentration by a known amount). When we test the sample and then the matrix spike, the matrix spike result should be higher by that known amount added. If the analytical procedure is not working well for our sample, the matrix spike result will be higher or lower than we expect.

CHAPTER FOUR

4. Result and Discussion

4.1. Instrument Calibration

Atomic Absorption Spectrophotometer (Model ZEENIT 700P) was used to determine the metal concentrations in the water sample. Instrument calibration was done using the standards before determination of the sample. The stock solution, that is 1000 ppm of each metal, was taken and 10 ppm was prepared as an intermediate for preparing the working standards. The working standards were prepared according to the sensitivity of each lamp in the AAS instrument. By using the working standards the instrument was calibrated with good correlation coefficient. After making sure the instrument was properly calibrated, the concentration of the metals in each sample was measured.

The linear correlation graph for each metal standards are described as shown in the following figures in absorbance Vs concentration (mg/L)

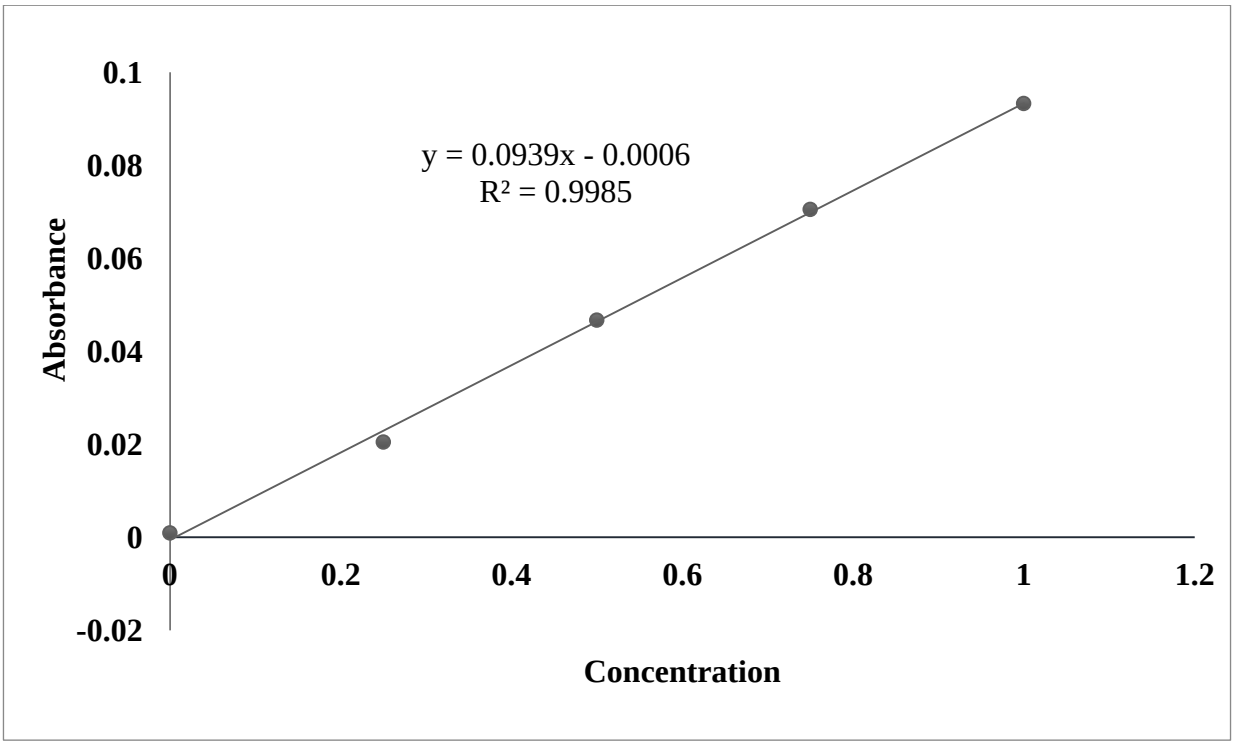


Figure 4.Calibration graph of Zinc

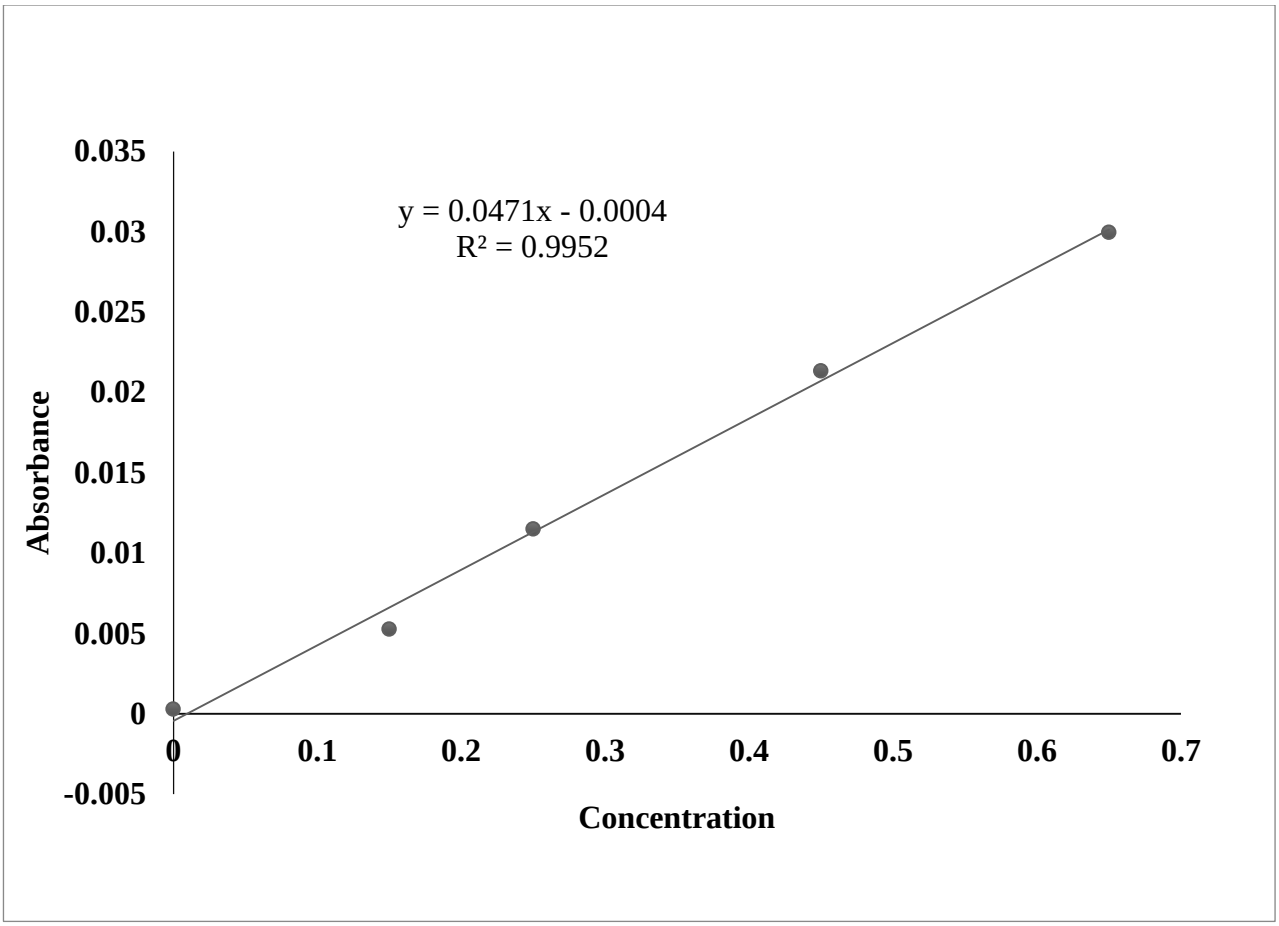


Figure 5. **Calibration graph of Cadmium**

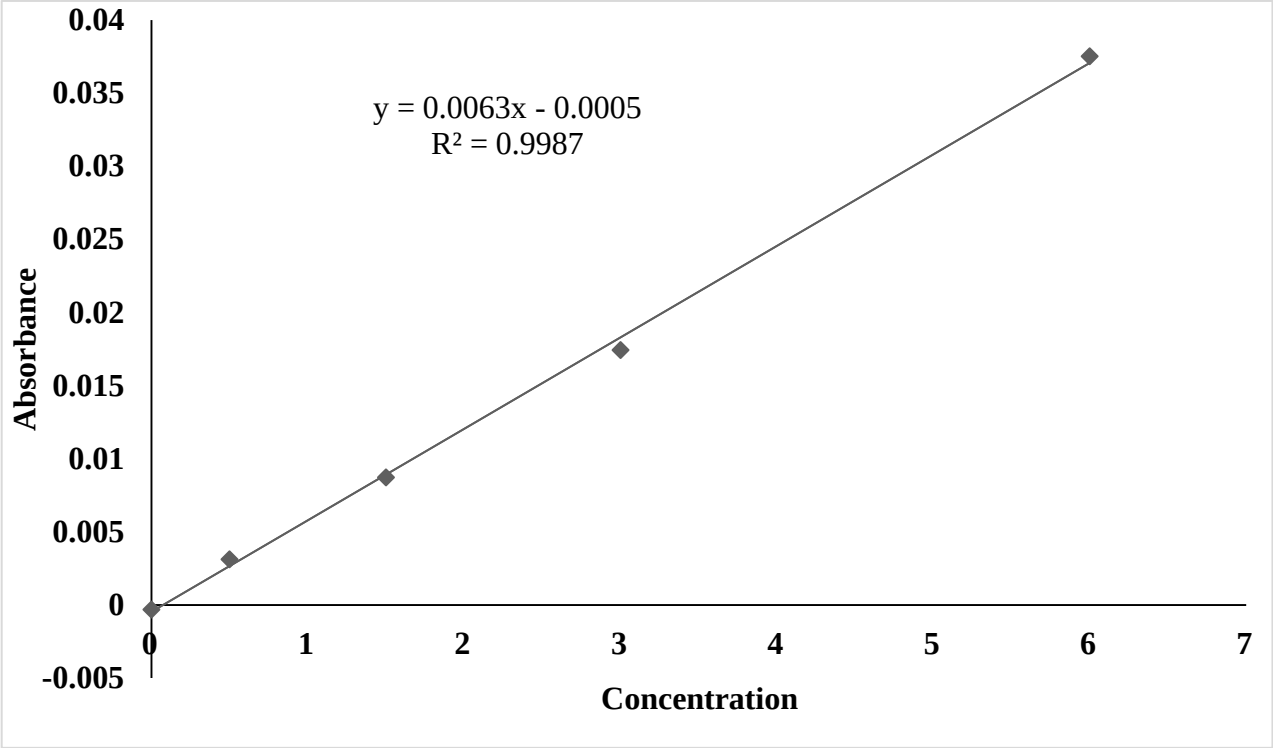


Figure 6. Calibration graph for Nickel

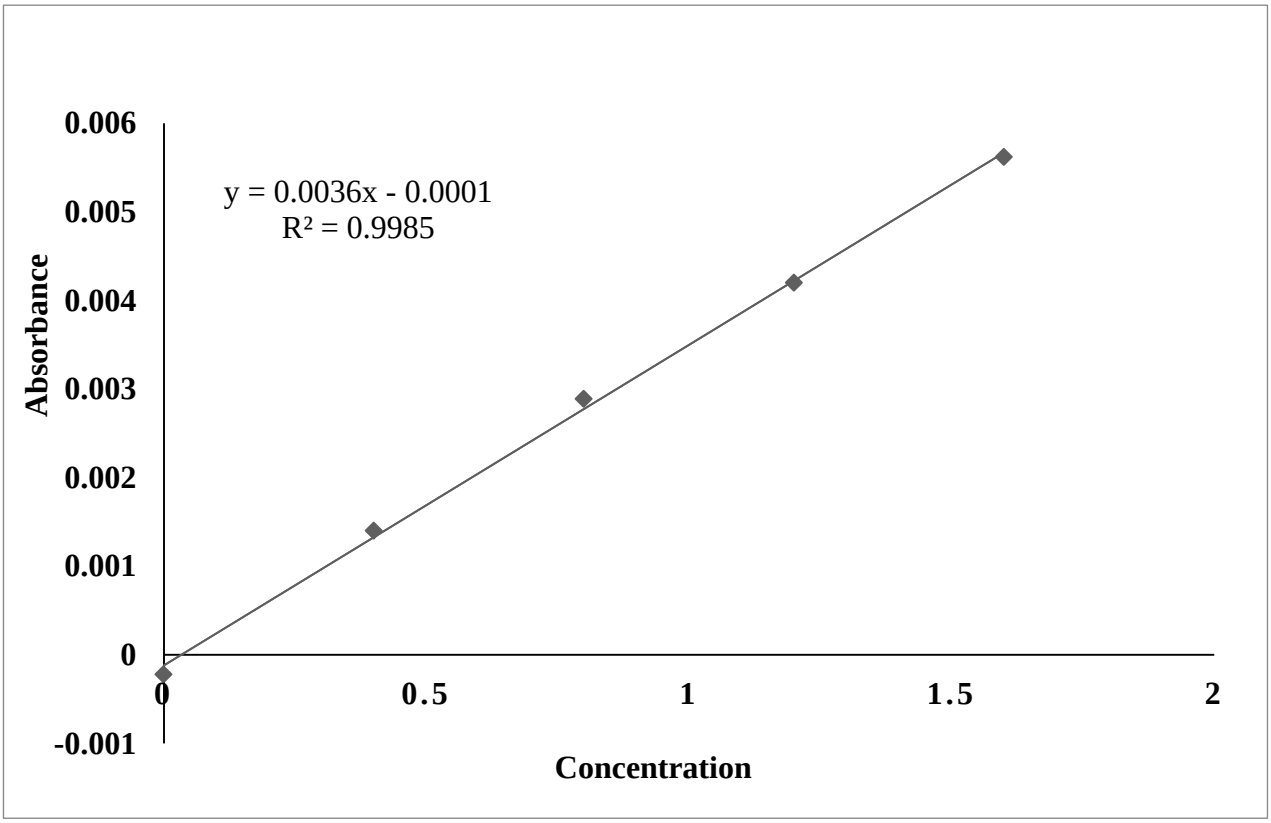


Figure 7.Calibration graph for Lead

Table 3. Concentration of standard solution used to calibrate the instrument and their corresponding correlation coefficients for the determination of the metal

Metals	Conc. of stock solutions (mgL^{-1})	Conc. of intermediate solution (mgL^{-1})	Conc. of standard series (mgL^{-1})	Correlation coefficient
Zn	1000	10	0, 0.25, 0.5, 0.75, 1	0.9985
Cd	1000	10	0, 0.15, 0.25, 0.45, 0.65	0.9952
Ni	1000	10	0,0.5,1.5,3,6	0.9987
Pb	1000	10	0,0.4, 0.8, 1.2, 1.6	0.9985

4.2. Method Detection Limit

Method detection limit is the minimum concentration of the analyte which can be detected at 99% confidence level. Detection limit of a certain method may vary greatly often with matrix and experimental procedure (Ewing). In this study Method detection limit of each metal was estimated by digesting three analytical blanks for both Akaki and control Holeta water. Each blank solution was also determined with FAAS at the same time and condition as with the samples. The standard deviation of the blank were determined to calculate MDL.

$$MDL = 3\times\boldsymbol{\delta}$$

$\boldsymbol{\delta}$ = Standard deviation of the blank

Table 4.Method detection limit of the metals

Metal	Zn	Ni	Cd	Pb
MDL(mg/L)	0.22	-	-	-

As shown in the above table, the MDL is low enough to detect the presence of metal at trace level in both Akaki and Holeta water.

4.3 Method Validation (Recovery Test)

The validity of the method was assessed by spiking samples with standards of known concentrations and calculating percentage recoveries. The percentage recovery for the metals are given below in table 5. These values were within the acceptable range of 80 to 120% expected for the elements indicating good accuracy of the analytical procedure (Duanet al., 2003). The percentage recovery was calculated by using the following formula (S. S. Fong *at; al,* 2006).

$$\%\ Recovery = \frac{C(spiked) - C(non - spiked)}{C(added)} \times 100\%$$

Where: C(spiked) is metal content of the spiked sample

C(non-spiked) metal content of non spiked sample

C(added) is metal content of known concentration added

Table 5. **Recovery values of metals for the analyzed water sample**

Concentration(mg/L)				
Metal	Un-spiked sample	Spiked amount	Measured amount	Percent recovery
Zn	5.8 ± 0.26	1.16	6.92 ± 0.33	96.55± 2.63
Ni	0.4802 ± 0.072	0.2401	0.7031 ± 0.06	92.83± 2.68
Cd	0.0110± 0.002	0.00555	0.0163 ± 0.0014	93.69± 10.91
Pb	<0.03	0.8	0.7766 ± 0.06	97.07 ± 7.63

- concentrations in spiked and un-spiked sample are calculated by mean ± SD of the triplicate readings of triplicate sample.
- percent recoveries are calculated by mean ± SD of percentage recoveries of triplicate readings of triplicate samples.

According to the above table the percentage recovery ranged from 92% to 98%. This indicates that the method used to determine the metals from waste water is in the acceptable range and valid.

4.4. Concentration of Heavy Metals in Akaki and Holeta Water

Akaki and control Holeta water samples were analyzed for heavy metals in dry season, October and December, and the results are presented below.

4.4.1. Concentration of Heavy Metals

Water samples were obtained from 5 (five) sampling sites in both Akaki and Holeta rivers in two consecutive Months and homogenized for FAAS determination. The mean ± SD level of Pb, Ni, Zn, and Cd obtained are presented in the table below.

Table 6. **Mean concentration (mg/L) of heavy metal in water sample**

Metals	Akaki (mg/L)	Holeta(mg/L)
Zn	5.82 ± 0.32	0.82 ± 0.07
Ni	0.4802 ± 0.072	BDL
Cd	0.0111 ± 0.002	BDL
Pb	BDL	BDL

During these analysis time, the water was found to contain Nickel and Cadmium in Akaki and Zinc in both rivers. But the other heavy metals studied existed blow detection limit of the instrument and method detection limit.

4.5. Comparison of Metals in Akaki with Holeta Water

Metals are persistent in the environment if once released to the environment and tend to bio accumulate in plants, organisms, and even become biomagnified in the food chain where human beings are highly exposed (Nabrzyski and Reilly; 2006). Both Akaki and Holeta rivers are excessively used for irrigation to cultivate different grains and vegetables and even for drinking. So, if the water is polluted with heavy metals, the metals will be transferred to animals and humans immediately. When the metals are compared in the two rivers, some metals are present in higher amounts in Akaki than in Holeta river.

The level of Zinc determined was 5.82 ± 0.32 and 0.82 ± 0.07 mg/L in Akaki and Holeta river respectively. So, Zinc occurs in higher amount in Akaki than in Holeta river

The level of Nickel determined was 0.4802 ± 0.072 mg/L in Akaki river and below detection limit in Holeta water, that is, the amount of Nickel is higher in Akaki than in Holeta water.

The level of Cadmium determined was 0.0111 ± 0.002 mg/L in Akaki river and below detection limit in Holeta water, that is, the amount of Cadmium metal is higher in Akaki than in Holeta water. The level of Lead is below detection limit for both Akaki and Holeta river.

Zinc, cadmium, and Nickel are higher in Akaki than in Holeta river due to large amount of contamination by waste from industries and household compared to Holeta. So, Holeta water is more suitable for irrigation and drinking purposes than Akaki river.

4.6. Comparison of Metals in Akaki and Holeta Rivers with Literature Values and Guidelines

The levels of heavy metal (Zn, Cd, Ni, and Pb) in different rivers have been reported in different countries from different point of views like health problem, nutrition, for drinking water standard, etc. Some of the available data are presented in the table along with the data of this study and other Ethiopian rivers for comparison.

Table 7. **Comparison of metal concentrations with those reported in the literature(mg/L)**

Country	Water type (River)	Zinc (Zn)	Cadmium (Cd)	Nickel (Ni)	Lead (Pb)	Reference
India	Bellandur Lake (dry season)	0.13	-	0.0065	0.0033	Lokeshwa 2006
Nigeria	Borehole, Hang dug (surface water)	0.1 -0.34	-	0.15 - 0.28	-	Jatua, B.S 2008
Kenya	Mbagathi and Ruiru river (dry season)	0.016-0.055	0.001-0.010	0.020-0.040	0.004-0.035	Mwangi John 2009
Ethiopia	Lake Zeway	0.03-0.04	0.009-0.01	-	-	Nigussie
Ethiopia	Akaki river	5.82	0.0111	0.4802	-	This study
Ethiopia	Holeta river	0.897	-	-	-	This study

The mean levels of Zinc in Akaki and Holeta waters in the study are higher than those reported for metal levels in India (Lokeshwa, 2006), Nigeria (Jatua, 2008), Kenya (Mwangi, 2009), and Ethiopia (Nigussie, 2010).

The mean level of Nickel in Akaki is higher than those reported in the literature, but the amount of Nickel in Holeta river is less than the mean level of nickel reported in India, Nigeria and Kenya.

The mean level of Cadmium in Akaki river is higher than those reported in India and Nigeria but similar with Kenya and Ethiopia (studied in lake Zeway) reported in the literature, but the amount of Cadmium in Holeta river is less than the mean level of this metal reported in India, Nigeria, Kenya and even in Ethiopia(studied in lake Zeway).

The amount of Lead (Pb) in this study is below detection limit (BDL). Also, this metal is less than reported in Kenya and India. In the other countries lead is reported below detection limit like Akaki and Holeta waters.

Table 8. **Some guidelines for water quality (mg/L)**

Standard	Zn	Cd	Ni	Pb	Reference
Australia	2	0.01	0.2	0.2	Nassef M.
Pakistan	5	0.1	1	0.5	Nassef M.
WHO	3	0.003	0.02	0.01	GDWQI
Ethiopia	5	0.003	-	0.01	EDWS

The mean level of Cadmium in Akaki water is less than the standard of Pakistan and almost equal with Australia's guide line. But the concentration is higher than the guide lines of both WHO and Ethiopia.

The level of nickel obtained in this study in Akaki water is less than in Pakistan water quality standard and higher than Australia and WHO water level guidelines.

The level of Zinc obtained in Akaki river is almost equal with the standard in Pakistan and Ethiopia, but higher than WHO and Australia guidelines.

The mean level of lead obtained in Akaki river and all metals in Holeta river in this study are less than the guidelines or water reported in Australia, Pakistan, WHO, and Ethiopia.

CHAPTER FIVE

5. Conclusion and Recommendations

5.1. Conclusion

The concentration of Zinc, Cadmium, and Nickel in Akaki river are higher than Holeta river. This is because Akaki river is intensively used for Industrial and household waste disposal area.

The levels of Zinc, Cadmium, and Nickel obtained are also higher than most of guidelines or standards reported. This may expose to health risk for people living around the area of the river because the river is used intensively for irrigation and even for drinking purpose.

Except for lead, the amount of heavy metals obtained in Akaki river are not safe enough compared with the standard water level reported. The control water for this study is Holeta water, this water is free from heavy metal contamination according to the guidelines reported. So, Holeta river is more safe for irrigation and drinking purpose than Akaki river.

5.2. Recommendations

The time of study of this river was very short. It was difficult to access large sample from all areas of Akaki and Holeta rivers, and to collect samples during all seasons to have more a representative sample for the study. So, it is recommended for other researchers to take more time and more number of samples to address of this river to include the limitation faced in this study.

For people concerned, nowadays Akaki river is turning to waste disposal area specially for industries. As a result a large amount of heavy metals are released to the river and reach hierarchically to animal and human beings and become the cause for different diseases. This is because the river is largely used for irrigation to cultivate different crops and vegetables. So, the different factories planted around the river should be warned to release their waste after treatment.

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Declaration

1, The under signed declare that this project work is my original work under the supervision of my advisor in the faculty of science. Department of chemistry, AAU in the academic year 2017/2018 and it has not been submitted in this or any other university . All sources of ideas and materials are honestly acknowledged.

Name:- Bezabih Aderaw

Signature_____

This project work has been submitted for examination with my approval as university advisor.

Advisor's Name _____

Signature_____

Place and date of submission: April 2018