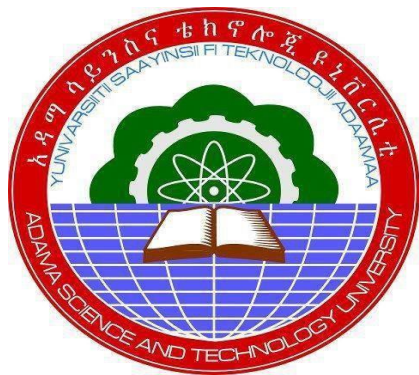




Analysis of Lake Beseka Water Using Inductivity Coupled Plasma Optical Emission Spectrometry (ICP-OES) Technique

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A thesis presented to the School of Post Graduate Program of Adama Science and Technology University in partial fulfillment requirements for the Degree of Master of Science in physics (Laser Spectroscopy)

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Adama, Ethiopia

APPROVAL SHEET

ADAMA SCIENCE AND TECHNOLOGY UINVERSITY

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This is to certify that the thesis prepared by Assefa Eba Horssa ,entitled “**Analysis of Lake Beseka water using Inductivity Coupled Plasma Optical Emission Spectromety(ICP-OES) Technique**” submitted in fulfillment of the requirement for the degree of Master of Science in Physics complies with the regulation of the University and meets the accepted standards with respect to originality. Signed by the examination committee

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DECLARATION PAGE

I hereby declare that this thesis entitled “Analysis of Lake Beseka water using Inductivity Plasma Optical Emission Spectrometry (ICP-OES)Technique”submitted for the Degree of Master of Science in Physics is my original work and the thesis has not formed the basis for the award of any degree, diploma or fellowship of similar others titles. It has not been submitted to any other University or institution for the award of any degree or diploma. All sources of materials used in this thesis are acknowledged properly.

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Date

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Abbreviations and Acronyms

B	Boron
Ca ²⁺	Calcium ion
Cl ⁻	Chloride ion
CSA	Central Statistical Authority
Cu	Copper
DEM	Department of Environmental Management
EC	Electric Conductivity
EHNRI	Ethiopia Health and Nutrition Research Institute
EPA	Environmental Protection Agency
FAAS	Flame Atomic Absorption Spectrometry
Fe	Iron
FMOH	Federal Ministry of Health.
GAAS	Graphite Atomic Absorption Spectrometry
HCO ₃ ⁻	Hydrogen Carbonate ion
ICP-OES.	Inductively Coupled Plasma Optical Emission Spectrometry
IMAC	Interim Maximum Acceptable Concentration
IRZ	Initial Radiation Zone
IWRM	Integrated and holistic approach of water Resources Management
K ⁺	Potassium ion
LOD	Limit of Detection

MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MDG	Millennium Development Goal
Mg ²⁺	Magnesium ion viii
Mn	Manganese
Mo	Molybdenum
Na ⁺	Sodium ion
NH ₄ ⁺	Ammonium
NO ₃ ⁻	Nitrate ion
NOAEL	No-Observed-Adverse-Effect Level
NRZ	Normal Radiation Zone
P	Phosphorus
PH	Power of hydrogen
PHZ	Preheating Zone
RHB	Regional Health Bureau
SMCL	Secondary Maximum Contamination Level
S ₂ O ₄ ²⁻	Sulfate ion
RF	Radio Frequency
TDS	Total Dissolved Solid
UNDP	United Nation Development Program
US	United State

USA	United State of America
USEPA	United State Environmental Protection Agency
USN	Ultrasonic Nebulizer
WHO	World Health Organization
WWSED	Water Work Design and Supervision Enterprise
Zn	Zinc

Abstract

This study focuses on the analysis of Lake Beseka water to check whether it is potable and also could be used for irrigation. Thus health risk factors if it is consumed by human population and wild and household animals and plants living around the river are studied. Samples of water were taken from five surface sampling points distributed around Beseka Lake and from five sampling points on Awash River starting from the entrance point of the discharging water from Beseka Lake in to the river. The parameter studied were EC, pH, TDS, Fe^- , F^- , Al^{+3} , Cr^- , Cn , SO_4^{-2} , NO_3 and NH_4^+ . The values of the parameters were compared with respect to the maximum acceptable standard level (guide line value) of WHO (World Health Organization) for drinking water. The instrument used to determine the parameters were ICP-OES, PH meter, and conductometer. The outcome of this study reveals that the chemical and the physical properties of the lake is out of the WHO standards to be use both for drinking and irrigation purposes. As a result, the physical and chemical composition of the Awash River was found affected by the introduction of the water of Lake Bseka by letting it with drainage canal into the river. Finally, this study recommends possible options of solutions which minimizes the aggravation of the expansion of the lake and indicate preferable instrument of water quality monitoring process.

UNIT ONE

1. Introduction

Water is a basic element of life, key for food security, poverty reduction, economic growth, energy production and human health and a vital input to all aspects of production and economic activities, nature's most precious resource and an essential necessity for the operational of our ecosystems. It has been an important issue in the development of human civilization in general and central to Ethiopia's growth ^[1].

The significance of water on agricultural production and industrial development and other life support activities or livelihoods is soundly crucial. Further, it is needed in all aspects of life, so the government and people want to assure adequate water availability in quantity and quality to all people ^[2]. Water influences natural systems and human activities in the context river basin. Natural water systems are shaped by their physical basins, human use environmental changes and climate systems. As the earth's population and the resulting anthropogenic footprint and impaction on climate increase, the need to maintain and protect fresh water resources gains importance for sustainable development, balancing social needs with economic development and environmental stewardship

A comprehensive water resources monitoring and information system is importantly needed to follow-up and ensure every citizen get access to safe and adequate water to meet basic needs, since water is unfavorably related to the day to day socio economic activities. Due to this fact, there is increasing harmony in giving the sector the highest priority in the development agenda and national plan to water resources management approach to an Integrated and holistic approach of Water Resources Management (IWRM) at river basin level ^[3]. Nowadays the quality of water for drinking and for irrigation purposes is affected by human made or naturally happening processes. This study tries to identify to what extent the insurgence of Beseka's lake water into Awash River influences the quality of water needed for drinking as well as for irrigation.

1.1. Background of the study

The water intended for human consumption must be free from chemical and micro-organisms in amounts which would provide a hazard to health is universally accepted. Supplies of drinking-water should not only be safe and free from dangers to health but also be as aesthetically attractive as possible. Agricultural activities supplemented by irrigation also needs water free from unwanted concentration of salts. In most irrigation situations, the primary water quality concerns its salinity levels, since salt can affect both the soil structure and crop yield. However, a number of trace elements are found in water which can limit its use for irrigation.

Nowadays the quality of water for drinking and for irrigation purposes is affected by human made or naturally happening processes. Environmental waters are exposed to contamination by thousands of micro-pollutants from industrial, agricultural and natural origins. So that monitoring of water quality and its treatments is vital for human health and sustained agricultural activities in dry lands. The Federal Ministry of Health (FMOH) is responsible for water quality monitoring and following. The Department of Hygiene and Environmental Health is in responsibility of developing policy guidelines on water quality surveillance. The FMOH does not run its own water quality laboratory, but relies on facilities at the Ethiopian Health and Nutrition Research Institute (EHNRI). The FMOH mandates the Regional Health Bureau (RHB), which are mainly responsible for providing health-related services to the population, to carry out water quality surveillance in the regions ^[4].

Water on the Earth's surface is an essential part of the hydrological cycle. Water resources include surface waters, groundwater, lakes, inland waters, rivers, coastal waters, and aquifers. Monitoring lake dynamics is critical to favor sustainable management of water resources on Earth. Science and technology has made efforts to provide scientific measuring instruments that help the monitoring and inspection of water quality for drinking and irrigation. One of the instruments best for this purpose is an inductive coupled plasma-optical emission spectroscopy.

1.2. Statement of the problem

1.2.1. Location of Beseka Lake

Lake Beseka is located in the middle Awash River Basine, Central Rift Vally of Ethiopia at about 200km Southeast of the capital city, Addis Abeba. The lake is expanding as opposed to the other rift valley lakes in Ethiopia, which are shrinking ^[5]. It is an endoergic lake located at the northern extreme of MER just south of the Fentale volcano and is having an elevation of 953 a.s.l^[6]. Lake Beseka is one of the rift valley lakes near the Afar triangle. The lake plays an important role in the ecology of birds and wild life, as it is located in northern part of Awash National park.

1.2.2. Expansion of Lake Beseka and its problems

Lake Beseka has been ever expanding in volume as a result of which serious social, economic and environmental factors have been under threat. During the last four decades the lake level and surface have been increasing continuously. The height of the lake is also increasing. Before the establishment of the Metahara Sugar Estate in 1970's, according to the information from elders of the indigenous (Karaayyuu) people, the lake was like a small surface pond created during the rainy season and used as graining area and watering for their livestock during the dry season. Some study reports indicate that the lake expansion is due to the introduction of the Abadir and Nura Era irrigation which are discharging their irrigation excess directly into the lake. Others believed that it is the result of the geological changes happening [in the great African rift valley in general, and Ethiopian Rift Valley in particular ^[3,5]. According to the previous studies the lake was used to cover an area of 3km² up to the year 1964. By the 1972, the area coverage had reached 11 km². In 1998 its coverage was about 40 km² with maximum depth of 11m. The lake level and its areal coverage have been continuously increasing and currently proved to be a real danger to the environment at its vicinity and at its downstream. The real coverage of the lake to (Nov, 2010) is close to 50 km²^[5]. Lake Beseka has been expanding at an astonishing rate since the late 1960's and early 1970's. The area has increased from 3 to 40 km² within three and half decades. The average annual increment of the lake was 0.2m and the level of the lake has rose by 4m from 1976 up to 1997^[7]. The drastic expansion of the lake has led to many problems in the surrounding area and is a severe threat to the wellbeing of the indigenous people and the economic welfare of the nation in general. The situation would not be as such looming if the water could be used as drinking or irrigation water, but unfortunately the water is saline and alkaline. According to the previous

studies the following major problems has a determinant effect on the surrounding biological, hydrological, and infrastructural conditions. They are summarized as follows:

Beseka's drastic expansion

- Has had affected the highway and the railway structures which run along its northern shore by flooding the highway several times and block transportation and has forced the government to spent large money for repeated maintenance and then obliged to do new railway and highway construction far away from the older course.
- Has had caused the loss of more than 57 human lives due to its flooding over some part of Metahara Town and Addis Ketema Town whole ^[7].
- It has inundated about 35km² the nearby grazing land and displaced above 910 people ^[7].
- The nearby Awash National Park has been affected indirectly, as displaced nomads encroached into the park, looking for grazing land ^[7].
- So that the Awash National Park area has reduced from an original 750km² to the current size of 250km², and caused the local nomadic pastoralists to move their camels and cattle into the national park for grazing ^[7].
- The expanding lake has reached in less than 3km from the Awash River, which is the source of drinking water and irrigation for millions of people downstream.
- Has affected the surface and the ground water dynamics and soil properties of the region. This increases the salinity of the soil near by the lake by interfering with the production and productivity of the Sugar Plantation ^[5].

After a different studies made on Beseka's expansion properties the government and Water Works Design and Supervision Enterprise has taken different remedial measures. Among these measures, interception of the ground water and discharging of water from Lake Beseka into awash river in such a way that environmental requirements are strictly met so that significant drawdown in lake level could brought about and reclamations of previous submerged agricultural and grazing land is made practical besides, arresting the lake level

growth. And therefore the annual maximum design release of water from the lake is decided to be $2.38\text{m}^3/\text{s}$ that can be released in the first year of the given period ^[6].

Based on these remedial measures taken place, this research aims to find out:

- weather the decision given to discharge the Beska's water into the Awash River as a solution to halt its expansion were taken place in a proper manner without perturbing the environmental requirements or not.
- Weather discharging of Beseka's saline water has brought unexpected influences on the chemical and physical properties of Awash River, which is the main source of water for drinking and irrigation used by the downstream population human being and animals, or not.

1.3. Objectives of the study

1.3.1. General objectives

The general objectives of this research is to indicate how much negative effects are brought on the water quality of Awash River due to the discharging of Beseka's Lake water into it and show by how much degree of contamination for those governmental and nongovernmental organizations and make them to give immediate concern to the problems and take uninterrupted supervision on the released alkaline and saline water and then decrease the hazard of Beseka's saline water for drinking and for irrigation supplied to the population living in vicinity of the lake and downstream of the Awash River.

1.3.2. Specific objectives

This research, therefore, aimed

- To determine chemicals and their concentration level, pH values and EC of water of Beseka Lake.
- To compare the concentration of those chemicals, pH values and EC with that of standards (guide line value) put for the water of Lake Beseka.
- To find out whether the chemical content of the Lake Bseka's discharged water entering to Awash River is found at its dangerous level or not.

- To suggest possible recommendations' that give alarming message for whom It may concern.

1.4. Scope of the study

To get complete and precise information about the chemical, biological, and physical properties of the water of Lake Beseka as a whole. But, the biological study this is beyond the scope of this study due to financial, personal expertise and time constraints.

1.5. Limitation of this study

This research is limited to only finding the content of inorganic elements and compounds as well as some of the major chemical properties of the water discharged from Lake Beseka in order to describe the amount of its toxicity, salinity and alkalinity then show its impact on the change of property of water in the Awash River. It was proposed to analyze about 25 chemical substances in addition to pH, EC, and TDS, of Lake Beseka and Awash River. Among them only eight chemical substances were investigated due to the shortage of suitable chemical reagents and scarce of money to buy the wanted but the expensive chemical reagents.

1.6. Significance of the study

The Awash, a major Ethiopian river emanating from a high plateau near Ginchi town, about 80km west of Addis Abeba and, after 2000km, emptying into Lake Abbe in the Denakil depression, runs south-east of Lake Beseka's water divide. Its catchment area of 110,000km² and serves as home to 10.5 million of inhabitants ^[7]. Along its way many tributary rivers, hot springs and other human discharges mix with its water. The chemical composition of water flowing along its course varies significantly as many studies show. This research paper is intended to show impacts of Beseka's lake saline water entering Awash River upon the quality of potable water and water for irrigation consumed by the populations living around the river near by the lake and downstream of the Awash River.

1.8 Organization of the study

In unit one, the introduction and the background statement of the research are given then the statement of the problem is elaborated concerning the effect of the withdrawal of Lake Beseka on the quality of water needed. Based on the problems mentioned in the above the general and the

specific objectives of this thesis are formulated. Next, the scope and the limitation of the research covering is also explained. Under chapter two reviews of related literatures of the research is given. In chapter three, the methods, procedures, materials needed to accomplish the research are written. Beneficiaries who are benefited from the findings and results of this research are indicated. Then the references taken from different related research results are mentioned at the end.

UNIT TWO

2. Literature review

2.1. Water and human health

Water is the most important nutrient for our body. It performs numerous important biological functions in the body. Moreover, use of safe drinking water can make massive contribution to health, productivity, social development, important to improved child health and mortality reduction ^[8]. Furthermore, according to Millennium Development Goal (MDG) wise utilization of water resources is becoming very important for poverty reduction and social development as world faces water crises which could hold back human development particularly in Sub-Saharan Africa ^[9].

According to the United Nations Development Program (UNDP) many people in developing countries continue to rely on unimproved water sources which are nearly one-sixth of the world's population obtains drinking water from unimproved sources, and in many developing areas, progress in expanding clean water coverage is modest ^[10]. Although the MDG drinking water target refers to sustainable access to safe drinking water, the MDG indicator “use of an improved drinking water source” does not include a measurement of either drinking water safety or sustainable access. This means that accurate estimates of the proportion of the global population with sustainable access to safe drinking water are likely to be significantly lower than estimates of those reportedly using improved drinking water sources. It is likely that many hundreds of millions more will still lack sustainable access to safe drinking water. The world is on-track to meet the MDG water target based on the indicator “use of an improved drinking water source” but, at the current rate of progress, this still will leave 672 million people without access to improved drinking water sources in 2015 ^[11].

Although, Ethiopia has made an encouraging growth as access to safe drinking water has increased for rural and urban areas, still Africa is lagging behind the achievement of the MDG due to lack of access to safe drinking water with the same author.

2.2. Water quality

Water quality is determined by contents in water modified from “World of fresh water”. The United State (US) Environmental Protection Agency (EPA) has established drinking water standards for public water supplies, the drinking water standards are divided into two types of standards. The primary drinking water standards were set based on specific health concerns or impacts; whereas the secondary drinking water standards are based on aesthetic issues and concerns. The primary drinking water standards are also known as Maximum Contaminant Level (MCL) and the secondary drinking water standards are known as Secondary Maximum Contaminant Levels (SMCL) [8].

In addition to the regulated standards, stated by the same author, the EPA also provides recommended non enforceable exposure limits. Maximum Contaminant Level Goals (MCLG) are non-enforceable limits established by the EPA that are based on possible health risks over a lifetime of exposure. EPA proposes regulations that bound to the amount of certain impurities in the water provided by public water systems for tap water. At last water quality depends on the local geology and ecosystem, as well as human activities.

2.3 Water Quality Parameters

2.3.1. pH Value

The pH is a measure of the acidity or basicity of a solution and its test is one of the most common analyses in water testing. The term “pH” is a mathematical transformation of the hydrogen ion (H^+) concentration; it conveniently expresses the acidity or basicity of water. The lower case letter “p” refers to “power” or exponent, and pH is defined as the negative logarithm of the hydrogen ion concentration. Each change of one pH unit represents a ten-fold change in hydrogen ion concentration. The pH scale is usually represented as ranging from 0 to 14, but pH can extend beyond those values. At 25 °C, pH 7.0 describes the neutral point of water at which the concentrations of hydrogen and hydroxyl ions (OH^-) are equal (each at 10^{-7} moles/L). Conditions become more acidic as pH decreases and more basic as pH increases. In fact, its measurements are on a scale run from 0 to 14, with 7.0, below 7.0 and above 7.0 deliberated as neutral, acid and base respectively and pH of most fresh water lies within the range 6.5–8.5^[12]. Water with a pH of less

than 4.8 or greater than 9.2 can be harmful to aquatic life. Most freshwater fish prefer water with a pH range between 6.5 and 8.4. The pH is also a useful indicator of the chemical balance in water. A high or low pH will adversely affect the availability of certain chemicals or nutrients in the water for use by plants.

The pH scale is logarithmic,

$$pH = -\log H^+ \dots\dots\dots 1$$

The pH of water can be affected by numerous factors, including biological availability and solubility of elements in water that can result in a significant increase or decrease in pH levels of water [11].

2.3.2 Electrical Conductivity (EC)

Conductivity defines the ability of an aqueous solution to carry an electric current. Although this parameter does not provide information about specific chemicals in water, it acts as a good indicator of water-quality problems [13].

$$\text{Conductivity } (K) = \frac{\ell}{RA} \dots\dots\dots 2$$

The resistance (R) of the electrolyte is measured across two plates with area (A) immersed in the liquid and held at a fixed distance (ℓ) apart in a conductivity cell. Conductivity in water that reported in micro Siemens per centimeter ($\mu\text{S}/\text{cm}$), is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, iron, aluminum cations (ions that carry a positive charge) and organic compounds like oil, phenol, alcohol, sugar, those do not conduct electrical current very well. Pure water is not a good conductor of electric current rather a good insulator.

Increase in ions concentration enhances the electrical conductivity of water. Generally, the amount of dissolved solids in water determines the electrical conductivity. Electrical conductivity (EC) is actually measures the ionic process of a solution that enables it to transmit current. According to WHO standards EC value should not exceeded $400\mu\text{S}/\text{cm}$ [14]. Moreover it is

affected by temperature: the warmer the water, the higher the conductivity. The change in conductivity per degree Celsius as a function of temperature (the first derivative) for sea water appears to be a linear function of temperature.

$$\frac{dk}{dh} = 23.54 + 0.1536T \dots\dots\dots 3$$

Integrating equation (3) becomes

$$K = 774.1 + 23.54T + 0.07680 T^2 \dots\dots\dots 4$$

Equation (4) agrees to within about 0.13 percent with the four measurements by Harned and Owen at 0, 18, 20, and 25 °C. It thus appears to be satisfactory over the temperature range of interest in natural waters based on the above author.

2.3.3. Total Dissolved Solids (TDS)

Water has the ability to dissolve a wide range of inorganic and some organic minerals or salts such as potassium, calcium, sodium, bicarbonates, chlorides, magnesium, sulfates etc. These minerals or salts such as potassium, calcium, sodium, bicarbonates, chlorides, magnesium, sulfates, etc. These minerals produced unwanted taste and diluted color in appearance of water that exceeds the WHO standard limit of 1000ppm. Total dissolved solids (TDS) in drinking water originates in many ways from sewage to urban industrial waste water etc. Therefore, TDS test is considered to a sign to determine the general quality of water^[7].

2.3.4. Turbidity

Turbidity, like transparency, is a measure of water clarity (how far light can travel through water). The more particles suspended in a sample of water, the more difficult it is for light to travel through it and the higher the water's turbidity, or murkiness. Although the suspended particles that reduce clarity can include organic particles (microbes, algae and plant particles, and animal detritus) as well as inorganic particles (silt and clay particles), turbidity in the Red River is usually a measure of the inorganic particles that account for most of the total suspended solids (TSS). Turbidity is measured by an instrument called a nephelometer and is reported in nephelometric units

(NTUs).The nephelometer, also called a turbidimeter, has a photocell similar to the ones used in cameras to indicate when the "flash" is needed. The water sample is placed in a column in the instrument, and the photocell reads the intensity of a beam of light showing through the water column. The cloudier or more turbid the water, the lower the intensity of the light that reaches the photocell and the higher the NTUs. High TSS or the presence of dark-colored humic acids from the decay of vegetation, common in the water of peat bogs, would result in a high turbidity reading [15].

2.3.5. Color of the water

Water usually thought to be a colorless liquid, however possesses some level of color. Colors in ground waters can originate from decomposition of organic matter and leakage through sewage. It was possibly due to suspended minerals and dead organic matter [8].

2.3.6. Taste of the Water

Various odors and tastes may be present in water. Taste is generally classified in three groups: sweet, medium and brackish. Taste in water can be traced to a number of factors including decaying organic matter, living organisms, iron, mixing industrial waste etc. [14]

2.3.7. Chemicals

Sodium: is essential for normal functioning of the human body and it can be found in all body tissues and fluids. The Ontario Drinking Water Systems Regulation 170/03 under the Safe Drinking Water Act 2002 requires reporting to the local Medical Officer of Health when sodium levels in public drinking water supplies exceed 20 mg/l. The visual objective for sodium in drinking water is ≤ 200 mg/l, as were reported human body needs sodium in order to keep blood pressure, control fluid levels and for normal nerve and muscle function [16].

Potassium: is a useful element in all animal and plant tissues. Individuals most at risk are primarily those in which excretion of potassium ions might be reduced or compromised, including those with kidney disease or renal insufficiency, older individuals who have reduced physiological reserve in their renal function, as well as individuals with other conditions (heart disease, coronary artery disease, hypertension, diabetes, adrenal insufficiency and existing hyperkalemia) and/or individuals who are taking medications that interfere with normal potassium-dependent functions

in the body. In addition, infants may also be more exposed because of a limited renal reserve and immature kidney function ^[17].

Magnesium: is an element that is critically involved in cardiac and vascular function. Small changes in concentrations have significant effects on cardiac excitability and on vascular tone, contractility, reactivity and growth. Increased concentrations of extracellular magnesium cause vasodilatation, improve blood flow, decrease resistance, increase capacitance function of peripheral, coronary, renal and cerebral arteries and attenuate agonist-induced vasoconstriction, whereas decreased concentrations cause contraction, potentiate agonist-evoked vasoconstriction and increase vascular tone ^[4].

Fluoride: At concentrations greater than 1.0 mg/L, fluoride will reduce the incidence of dental cavities. At concentrations greater than 1.5 mg/L, fluorosis (mottling) of teeth may occur. Most municipal water supplies have added fluoride to reach the optimal level of 1.2 mg/L to reduce cavities.

Calcium: is found in bones and teeth, where it roles as a key structural element. The remaining body calcium functions in metabolism, serving as a signal for vital physiological processes, including vascular contraction, blood clotting, muscle contraction and nerve transmission. Inadequate intakes of calcium have been associated with increased risks of osteoporosis, nephrolithiasis (kidney stones), colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity ^[18].

Copper: water can react with copper to dissolve small amounts of copper into the water supply. Individuals who consume this water can be exposed to elevated levels of copper. Raised levels of copper for 14 days or more can lead to health problems such as permanent kidney and liver damage in infants under the age of 1 year. Copper can collect in these individuals to dangerous levels and, if not detected and treated, can cause death. The U.S. EPA has set the MCL for copper at 1.3 mg/l, which also may be reported as parts per million (ppm). Its levels in running or fully flushed water tend to be low, whereas those in standing or partially flushed water samples are more variable and can be substantially higher (frequently > 1mg/l).

The 1958 WHO International Standards for Drinking-water suggested that concentrations of copper greater than 1.5 mg/l would markedly impair the portability of the water. The 1963 and 1971 International Standards retained this value as a maximum allowable or permissible concentration. In the first edition of the Guidelines for Drinking-water Quality, published in 1984, a guideline value of 1.0 mg/l was established for copper, based on its laundry and other staining properties. The 1993 Guidelines derived a provisional health-based guideline value of 2 mg/l for copper. Copper can also give rise to taste problems at concentrations above 5 mg/l and can stain laundry and sanitary ware at concentrations above 1 mg/l. Guideline value 0.0006 mg/l. Occurrence has been detected in surface water and ground water, usually at concentrations of a few micrograms per liter, although levels as high as 1.3 and 3.5 mg/l have been measured in surface water and groundwater, respectively [19].

Aluminum: is the most abundant metallic element and constitutes about 8% of the Earth's crust. It occurs naturally in the environment as silicates, oxides, and hydroxides, combined with other elements, such as sodium and fluoride, and as complexes with organic matter. Use of aluminum salts as coagulants in water treatment may lead to increased concentrations of aluminum in finished water. Where residual concentrations are high, aluminum may be deposited in the distribution system. Disturbance of the deposits by change in flow rate may increase aluminum levels at the tap and lead to undesirable color and turbidity (WHO,1996). Concentrations of aluminum at which such problems may occur are highly dependent on a number of water quality parameters and operational factors at the water treatment plant. Acid environments caused by acid mine drainage or acid rain can cause an increase in the dissolved aluminum content of the surrounding waters [46].

Iron: (as Fe^{2+}) concentrations of 40 $\mu\text{g/L}$ can be detected by taste in distilled water. In mineralized spring water with total dissolved solids content of 500 mg/l, the taste threshold value was 0.12 mg/L. In well-water, iron concentrations below 0.3 mg/l were characterized as unnoticeable, whereas levels of 0.3–3 mg/l were found acceptable. In drinking-water supplies, iron (II) salts are unstable and are precipitated as insoluble iron(III) hydroxide, which settles out as a rust-colored silt. Although turbidity and color may develop in piped systems at iron levels above 0.05–0.1 mg/l, various iron salts are used as coagulants in water treatment. Dissolution of the median iron

concentration in rivers has been reported to be 0.7 mg/l. Concentrations of iron in drinking-water are normally less than 0.3 mg/L but may be higher in countries where various iron salts are used as coagulating agents in water-treatment plants and where cast iron, steel, and galvanized iron pipes are used for water distribution. Drinking-water containing 0.3 mg/l would contribute about 0.6 mg to the daily intake [20].

Chromium: is widely distributed in the earth's crust. It can exist in oxidation states of +2 to +6. Soils and rocks may contain small amounts of chromium, almost always in the trivalent state. In water, chromium(III) is a positive ion that forms hydroxides and complexes, and is adsorbed at relatively high pH values. In surface waters, the ratio of chromium(III) to chromium(VI) varies widely, and relatively high concentrations of the latter can be found locally. In general, chromium(VI) salts are more soluble than those of chromium(III), making chromium(VI) relatively mobile. The average concentration of chromium in rain water is in the range 0.21g/liter[48,49]. Natural chromium concentrations in sea water of 0.04-0.5µg/liter have been measured. The natural total chromium content of surface waters is approximately 0.5- 2µg/liter and the dissolved chromium content is 0.02 -0.3µg/liter[48,50,51]. Ingestion of 1-5 g of "chromate" (not further specified) results in severe acute effects such as gastrointestinal disorders, hemorrhagic diathesis, and convulsions. Death may occur following cardiovascular shock [52]. As a practical 0.05mg/liter, which is considered to be unlikely to give rise to significant risks to health, has been retained as a provisional guideline value.

Cyanide: can be determined in water by both titrimetric and photometric techniques, with detection limit of 2µg/liter. Cyanides are occasionally found in drinking-water, primarily as a consequence of industrial contamination. This results in a guideline value of 0.07 mg/L (rounded figure), which is considered to be protective for both acute and long-term exposure. Cyanide may lower vitamin B12 levels and hence exacerbate vitamin B12 deficiency. It has also been linked to an increased incidence of goiter (cretinism) in Zaire through effects on iodine uptake by the thyroid. Those with nutritional inadequacy or inborn metabolic errors are particularly vulnerable. Chronic effects on the thyroid and particularly on the nervous system were observed in some populations as a consequence of the consumption of inadequately processed cassava containing high levels of cyanide. This problem seems to have decreased significantly in the West African

populations in which it was widely reported following a change in processing methods and a general improvement in nutritional status.

Zinc: In natural surface waters, the concentration of zinc is usually below 10 µg/l, and in ground waters, 10–40 µg/l. In tap water, the zinc concentration can be much higher as a result of the leaching of zinc from piping and fittings. The median zinc content in water samples taken upstream and downstream of the water works was below 20 µg/l; much higher concentrations were found in tap water, the highest being 1.1 mg/l. Even higher zinc concentrations (up to 24 mg/L) were reported in a Finnish survey of water from almost 6000 wells ^[18].

Manganese: Potassium permanganate is used as an oxidant for cleaning, bleaching and disinfection purposes. Average manganese levels in ambient air near industrial sources have been reported to range from 220 to 300ng/m³, whereas manganese levels in urban and rural areas without point sources have been reported to range from 10 to 70ng/m³. The United States Environmental Protection Agency estimated the average annual background concentration of manganese in urban areas to be 40ng/m³, based on measurements in 102 cities in the USA. Levels in fresh water typically range from 1 to 200 µg/l reported that a river water survey in the USA found dissolved manganese levels ranging from <11 to >51µg/l. At the median drinking-water level of 10µg/l determined in the National Inorganic and Radionuclide Survey described above.

An epidemiological study in Japan described adverse effects in humans consuming manganese dissolved in drinking-water, probably at a concentration close to 28 mg/l. The levels of manganese in the drinking-water of three different geographical areas were 3.6–14.6µg/l in the control area and 81–25 µg/l and 1800–2300µg/l in the test areas. Long-term drinking-water study in a northern rural area of Germany found no neurological effects of manganese at a level of at least 0.3 mg/L. In one area of Japan, a manganese concentration of 0.75 mg/L in the drinking-water supply had no apparent adverse effects on the health of consumers.

The average manganese concentration of the drinking-water of the exposed group was 0.241 mg/l compared with the control level of 0.04 mg/l. Inductively coupled argon–plasma optical emission spectrometry has also been used to measure manganese concentrations in biological fluids, water, waste products and air and has a detection limit of around 1–2 µg/l for. Colorimetric methods are

also used in water analysis and have detection limits of about 10 µg/l. Manganese concentrations in drinking-water are easily lowered using common treatment methods. Oxidation and filtration are usually adequate to achieve a manganese concentration of 0.05 mg/l in drinking-water [22].

Molybdenum: Is considered to be an essential trace element in both animals and humans. In a survey of finished water supplies in the USA, levels of molybdenum in drinking-water do not usually exceed 10 µg/l. However, in areas near molybdenum mining operations, the molybdenum concentration in finished water can be as high as 200µg/l at which No-Observed-Effect Level (NOAEL) for molybdenum in drinking-water but tap water concentrations as high as 580µg/l have been reported in Colorado. A guideline value of 007 mg/l which is consistent with the essential daily requirement for molybdenum [16].

Boron: Is well absorbed from the gastrointestinal tract in humans its concentrations usually widely and depend on the surrounding geology and wastewater discharge, for most of the world the concentrations of the boron judged to be below 0.5mg/l. Ingesting large amounts of boron over short periods of time can harm the stomach, intestines, liver, kidney, and brain [23].

Phosphorus: in the form of phosphate, the highest concentrations occur in food staffs like; nuts, beans, and grains. Because public water supplies contain little phosphorus and, it can be concluded that phosphorus levels in drinking water contribute only a negligible amount to the daily intake [24].

Chloride: In Rhode Island, the Department of Environmental Management (DEM) has set acceptable chloride concentration exposure limits for freshwater organisms at 860 ppm to prevent acute (immediate) exposure effects and at 230 ppm to prevent chronic (long-term) exposure effects. For drinking water, DEM has set a maximum contaminant level of 250 ppm chloride, which is the point at which water starts to taste salty [25].

Carbonate ion: The major form of alkalinity in natural waters; its source being the partitioning of CO₂ from the atmosphere and the weathering of carbonate minerals in rocks and soil. Alkalinity is a chemical measurement of water's ability to neutralize acids. Alkalinity is also a measure of water's buffering capacity or its ability to resist changes in pH upon the addition of acids or bases. Neither alkalinity nor acidity, have any known adverse health effects. But bicarbonate and carbonate may complex with other elements and compounds, altering their toxicity [26]

Ammonium: As specified in the terms of reference from the European Commission, ammonium has been found in drinking water at levels above 0.5 mg/l after filtering the tap water with the water filter cartridges. At a pH of 7.25, 99 % of the ammonia is ionized and hence present as ammonium ions in aqueous solutions. In ground and surface waters natural ammonium levels are usually below 0.2 mg/l. the additional exposure to ammonium from water at the concentration range of 0.5-5 mg/l is negligible and does not pose a risk to human health. Natural levels in ground waters are usually below 0.2 mg/l of ammonia. Surface waters may contain up to 12 mg/l ^[27].

Nitrate levels above the EPA Maximum Contaminant Level of 10mg/l NO₃- N or 45 mg/l NO₃ may cause methemoglobinemia in infants. Nitrate also exists in animal feeds and fodder. Drought-stressed forage plants commonly have high nitrate levels. These feeds can have an additive effect when consumed with high nitrate drinking water. The maximum contaminant level (MCL) in drinking water as nitrate (NO₃) is 45 mg/l, whereas the MCL as NO₃-N is 10 mg/l. The MCL is the highest level of NO₃ or NO₃-N that is allowable in public drinking water supplies by the U.S. Environmental Protection Agency (EPA). Do not let infants drink water that exceeds 10 mg/l NO₃-N. High nitrate levels in water can cause methemoglobinemia or blue baby syndrome, a condition found especially in infants less than six months ^[28]. Nitrate levels should not be higher than 10 mg/L if reported as nitrogen (N). High nitrate may cause methemoglobinemia (infant cyanosis or "blue baby disease") in infants who drink water or formula made from water containing nitrate levels higher than recommended. Adults can drink water with considerably higher concentrations than infants without adverse effects. Livestock water can contain up to 100 mg/L of nitrate as nitrogen, but young monogastric animals such as hogs may be affected at nitrate levels considerably less than 100 mg/L ^[11].

Sulfate no health based guide line is proposed for sulfate by WHO, however because of the gastrointestinal effect resulting from ingestion of drinking water containing high sulfate levels, it is recommended that health authorities be notified of sources of drinking water that contain sulfate concentrations in excess of 500mg/l ^[29].

2.4 Overview of Analytical Atomic Spectroscopy

The core objective of analytical atomic spectroscopy is to detect elements and measure their concentrations in various media. In fact, Spectroscopy is defined as the interaction of light and matter and has both physical and analytical applications. Commonly used techniques for determination of trace concentration of elements in sample is atomic spectrometry. The qualitative and quantitative information of sample can be obtained by absorbed or emitted electromagnetic radiation. Once atoms get energy via electromagnetic radiation or collision, they excited to further orbital state with higher energy state then the electrons relax to lower excited or ground state through collision and emission of light. The ionization potential used to dissociate atoms in to positive ions is different for different element. The energy difference between upper and lower energy level of radiative transition defines the wave length of radiation that involved in that transition.

The Planck's equation is

$$\Delta E = h\nu \dots\dots\dots 5$$

Where ΔE is energy difference, h is Planck's constant and ν is frequency of radiation.

But, $\nu = \frac{c}{\lambda}$

where c is speed of light in vacuum and λ is wavelength. So that,

$$\Delta E = h \frac{c}{\lambda} \dots\dots\dots 6$$

At last, atomic Spectrometry technique is useful due to every atom has its own characteristic energy level and unique wavelength. In ICP-OES the intensity of light emitted at specific wavelength used to determine the concentration of interested element. While the wavelength used to determine types of element [30].

2.5 Inductively Coupled Plasma - Optical Emission Spectrometry(ICP-OES)

2.5.1 History of ICP-OES

In 1752, 26-year-old Thomas Melville wrote his observation of bright yellow light emitted from a flame produced while burning the mixture of alcohol and sea salt which disappear for alcohol alone. However, it is said that it had not died a year later, Spectrochemical analysis might have gotten a much earlier start ^[34]. The ICP was industrialized for optical emission spectrometry (OES) by Fassel et al. at Iowa State University in the US and by Greenfield et al. at Albright & Wilson, Ltd. in the UK in the mid-1960. The first commercially available ICP/OES instrument was introduced in 1974 ^[23]. This resulted in a vast rise in acceptance for ICP-OES analysis, which allowed rapid scanning (and later sequential analysis) of large numbers of elements. It was widely accepted that ICP was a good ion source, since that time an ever increasing number of academic governmental and industrial researcher have jointed in the development of ICP ^[30].

2.5.2 Advantages of ICP-OES

Powerful, sensitive, and multipurpose techniques presently existing for elemental analysis is ICP-OES. It has a numerous range of application areas including environmental, geochemical, semiconductor, nuclear, chemical, clinical, and food analyses. Similarly, it is used for other applications in various scientific disciplines like, archaeology, environmental chemistry. The main advantages of this instrument over other chemical analysis techniques are its ability to achieve accurate and precise in measurements of multiple elements in a variety of samples. In addition, the technique offers very low detection limits and it can determine analyte concentration down to part-per trillion (ppb) levels reliant on the background signal and the element of interest. In most cases, these detection limits are 100 to 1000 times greater than that can be normally achieved by FAAS and GAAS ^[31].

Besides, the ability of ICP-OES to detect element signals from Li to U in the periodic table makes this a versatile technique for elemental analysis ^[25]. There are analytical benefits of the ICP over other excitation sources originate from its skill for efficient and reproducible vaporization, atomization, excitation, and ionization for a wide range of elements in various sample matrices which is mainly due to the high temperature, 6000–7000 K, in the observation zones of the ICP. This temperature is much higher than the maximum temperature of flames or furnaces (3300 K). The high temperature of the ICP also makes it accomplished of exciting refractory elements, and renders it less prone to matrix interferences. In addition, the ICP is an electrode less source, so

there is no contamination from the impurities present in an electrode material. Furthermore, it is comparatively easy to build an ICP assembly and it is inexpensive, related to some other sources [31].

2.5.3 Characteristics of ICP-OES

Ability of ICP for efficient and reproducible vaporization, atomization, excitation, and ionization for a wide range of elements in various sample matrices make it more analytical advantages over other excitation sources due to the high temperature, 6000–7000K, in the observation zones of the ICP and the maximum temperature of flames or furnaces (3300K) is much less than that of ICP. The high temperature of ICP less noisy and better able to handle liquid samples and makes ICP capable of exciting refractory elements, and renders it less prone to matrix interferences. In addition, it is relatively easy to build an ICP assembly and it is in expensive.

To sum up

- Considerable degree of ionization for many elements.
- Simultaneous multi element competence.
- Low back ground emission.
- Comparatively low chemical interference.
- Great stability leading to excellent accuracy and precision
- Excellent detection limits for most elements (0.1– 100ngm/L1)
- Wide linear dynamic range and
- Cost effective analyses are some of the most beneficial characteristics of the ICP [32].

2.5.4 Layout of a typical ICP-OES instrument

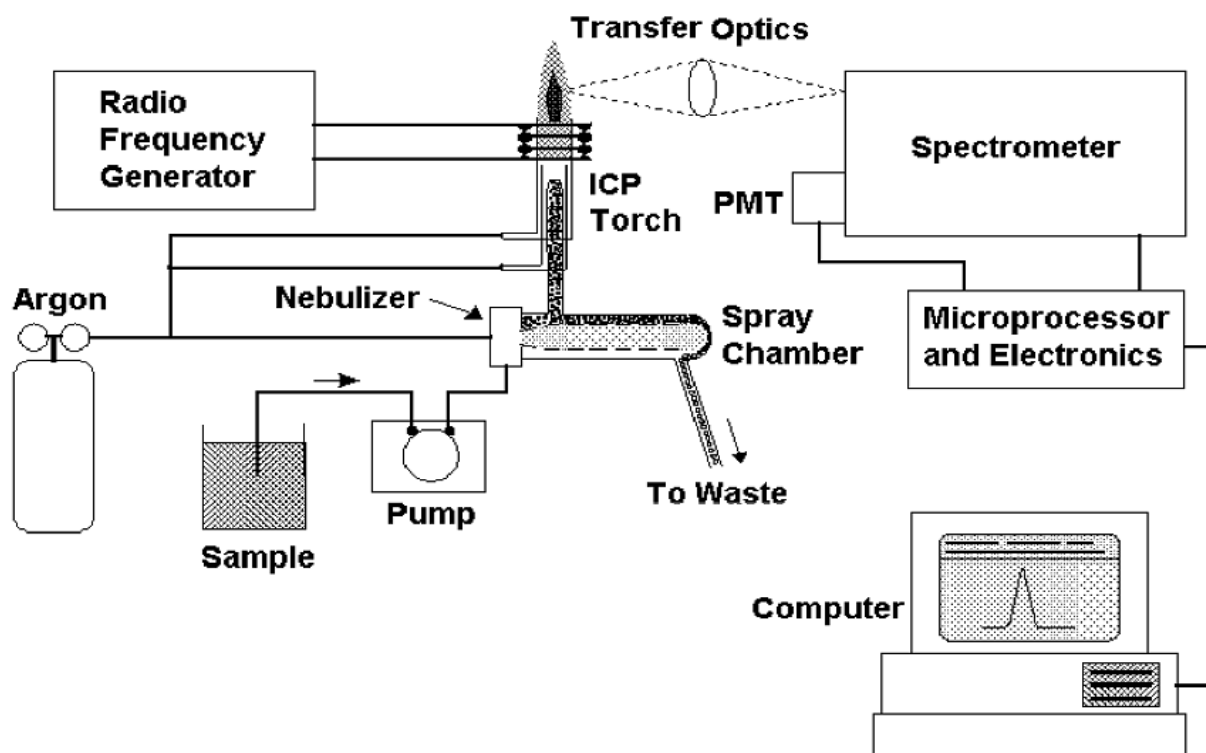


Figure 2.1. Major components and layout of a typical ICP-OES instrument. (Source: Charles B. Boss and Kenneth J. Concepts, *Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry*. The Perkin-Elmer Corporation, U.S.A.)

2.5.5 Principles of ICP-OES Operation

Operative temperature of an ICP is between 5000 and 10,000 K, which indicates desolvation and thermal atomization of analytes introduced into the central region of the plasma [33]. Liquid samples are pumped to a sample introduction assembly where they enter a nebulizer (in this work a concentric glass nebulizer was used) and are mixed with a high flow stream of argon gas, forming a fine aerosol. This means that aerosol formation and droplet selection in the spray chamber was carried out at room temperature, to avoid the possibility of drift from radiated heat inside the plasma compartment of the ICP-OES system. From the spray chamber, the smallest selected droplets pass to the central capillary tube of the glass torch located inside the ICP-OES. In fact, the ICP is generated as follows. RF power, typically 700–1500 W is applied to the load coil and an alternating current oscillates inside the coil at a rate corresponding to the frequency of the RF generator. The oscillation of the current at this high frequency causes the same high-frequency

oscillation of electric and magnetic fields to be set up inside the top of the torch. These ions and electrons are then accelerated by the magnetic field and collide with other argon atoms, causing further ionization in a chain reaction manner [34]. This process continues until a very intense, brilliant white, tear drop shaped, high-temperature plasma is formed. Adding energy to the plasma via RF-induced collision is known as inductive coupling, and thus the plasma is called an ICP [34].

$$B = \mu_o n I \dots\dots\dots 7$$

where B is magnetic field inside a solenoid

n is the number of turns per unit length.

I is the total current through a solenoid

$$E = \frac{\mu_o n I_{\max} \omega R}{2} \sin \omega \dots\dots\dots 8$$

where E is electric field induced by a changing magnetic field in a solenoid and a long solenoid of radius R has n turns of wire per unit length and carries a time-varying current that varies sinusoidally, as $I = I_{\max} \cos \omega t$ where $I_{\max}$ is the maximum current and ω is the angular frequency of the alternating current source [35].

The plasma power is typically operated at 1200 W, creates more free electrons. The resultant free electrons collide with other Argon atoms and sample molecules effectively atomizing and ionizing them. Solutions are typically nebulized into a spray chamber and the resultant aerosol is sent into the centermost tube of a quartz torch, where it is vaporized, atomized and ionized in the plasma and atoms are excited and ionized before leaving the plasma to enter the next stage of the instrument [30].

Once ionization have occurred which are the major mechanism in ICP by a number of processes like, collisions among ions, atoms and free electrons in the plasma those induce thermal ionization. The degree of ionization of an atom is affected by ion–atom and atom–atom collisions, where the energy required for ionization is derived from thermal agitation of the particles for a system is in thermal equilibrium. Boltzmann equations label how energy levels with atoms are populated.

Electrons may be jumping around but consider atoms as a statistical ensemble. This equation gives ratios of level populations as a function of temperature.

$$\frac{N_j}{N_i} = \frac{g_j}{g_i} e^{-\left(\frac{E_j - E_i}{KT}\right)} \dots\dots\dots 9$$

Where N_j is

The degree of ionization is dependent on the electron number density, the temperature and the ionization energy of the element. Then the degree of ionization as a function of first ionization energy, predicted by the Saha equation is given by

$$\left(\frac{n_{r+1}}{n_r}\right)n_e = \frac{G_{r+1}}{G_r} \frac{g_e}{h^3} \frac{(2\pi m_e KT)^{3/2}}{h^3} e^{-\frac{x_r}{KT}} \dots\dots\dots 10$$

where

- $n_{(r+1)}$ Density of atoms in ionization state $r+1$ (m-3)
- n_r Density of atoms in ionization state r (m-3)
- n_e Density of electrons (m-3)
- G_{r+1} Partition function of ionization state $r+1$.
- G_r Partition function of ionization state r
- m_e mass of electrons
- g_e Statistical weight of the electron
- h Planck's constant
- K Boltzmann constant
- T Temperature
- x_r Ionization potential of state r (to reach state $r+1$), ground level to ground level [34].

Advance excitation within the plasma imparts surplus energy to the atoms, encouraging them to excited states. Sufficient energy is often offered to transform the atoms to ions and subsequently stimulate the ions to excited states then relax to the ground state through the emission of a photon that have distinctive energies that are determined by the quantized energy level structure for the atoms or ions. Actually the total number of photons labels the concentration of element and the wavelength of the photons identifies the elements from which they originated. A portion of the photons emitted by the ICP is collected with a concave mirror and forms an image of the ICP on

the entrance aperture of a wavelength selection device such as a monochromator. The particular wavelength exiting the monochromator is converted to an electrical signal by a photo detector. The signal is amplified and processed by the detector electronics, then displayed and stored by a personal computer ^[36].

3.5.6. Calibration techniques and Standards

Calibration was carried out using working standards prepared from the Merck stock standards. The ICP-OES software used linear calibration curves to calculate individual element concentrations. The linear calibration curve which is established by assuming that the relationship between concentration (the X values) and intensity (the Y values) is linear and that the following equation describes this relationship:

$$y = mx + b \dots\dots\dots 11$$

where: x = concentration, y = intensity, m = slope of the calibration curve b = y-axis intercept ^[37]. The software automatically identified any result above the calibration range. The instrument software also measured the internal standard signals with each sample and automatically calculated and corrected for any drift that may have occurred during analysis from the original internal standard signal. At the end of the analysis run, the results file was then exported to Microsoft® Excel and Minitab® for manual processing ^[37].

2.6. Sampl introduction in to ICP-OES

A sample is transported into the central channel of the ICP as either a gas, vapor, aerosol of fine droplets, or solid particles, which is generated from a liquid sample by the use of a nebulizer. While entering the plasma, the droplets undergo three processes. Desolvation, or the removal of the solvent from the droplets, resulting in microscopic solid particulates, or a dry aerosol.

- Vaporization or the decomposition of the particles into gaseous state molecules.
- Atomization or the breaking of the gaseous molecules into atoms. These steps occur mostly in the Preheating Zone (PHZ). Finally, excitation and ionization of the atoms occur, followed by the emission of radiation from these excited species. These excitation and

ionization processes occur predominantly in the Initial Radiation Zone (IRZ), and the Normal Analytical Zone (NAZ) from which analytical emission is usually collected [38].

2.6.1. Peristaltic pumps

A peristaltic pump is a small pump with many mini rollers that rotate at the same speed. The purpose of the integrated peristaltic pump is to ensure a constant flow rate of the liquid sample from its container to the nebulizer. The peristaltic pump also allows for regulation of the sample uptake rate by varying the speed of the rollers. Moreover, the pump allows the operator to compensate for differences in the uptake rate due to differing viscosities of samples, standards, and blanks [34]. Bernoulli's equation is obtained by applying Newton's second law between two points on a streamline. It states that

$$P_1 + \frac{1}{2}\rho V_1^2 + \rho g Z_1 = P_2 + \frac{1}{2}\rho V_2^2 + \rho g Z_2 = C \quad \dots\dots\dots 13$$

where g is the gravitational constant, ρ is fluid density, Z_1 and Z_2 are the heights or elevations of points 1 and 2 above some horizontal reference plane, and P_1 and P_2 , and V_1 and V_2 , are the pressures and velocities at these same points, respectively. The applications Bernoulli's equation in both the peristaltic pump and spray leads to

$P_1 + \frac{1}{2}\rho V_1^2 + \rho g Z_1 = P_3 + \frac{1}{2}\rho V_2 + \rho g Z_3$, dividing both sides of the equation by ρ and substituting atmospheric pressure (P_{atm}) for P_1 will give

$$\frac{P_{Atm}}{\rho} + g Z_1 = \frac{P_3}{\rho} + \frac{1}{2} V_3^2 \quad \dots\dots\dots 13$$

Since V_1 and Z_3 are equal to zero. The momentum equation

$$\rho \frac{V^2}{R} = \frac{\partial P}{\partial n} + \rho g \frac{\partial z}{\partial n} \quad \dots\dots\dots 14$$

For steady, constant density flow without friction, across streamlines, as R becomes large and gravitation is ignored the pressure across straight streamlines is constant. As result

$$V_3 = \sqrt{2\rho g z_1} \quad \dots\dots\dots 15$$

This is the velocity of the water at the exit point of the peristaltic pump [39].

2.6.2 Nebulizers

Nebulizers are devices used to convert liquid sample into an aerosol and transported to the plasma. It is commonly used for solution sample introduction in ICP and the process is known as nebulization. Finely divided aerosol and argon gas that enters the nebulizer at the same time shears the liquid into very small droplets that pass through a spray chamber which removes all droplets, except those that are the right size and velocity for introduction into the plasma [33]. Actually, many forces used in ICP-OES to breakdown the liquid into aerosol but Pneumatic and Ultrasonic nebulizers (USNs) successfully used in ICP which efficient or high-speed as flows to create an aerosol and breaks liquid samples into a fine aerosol respectively. In addition, the pneumatic nebulizer retains its popularity owing to its suitability, reasonable stability, and ease of use.

Three types of pneumatic nebulizers are commonly employed in ICP.

- Concentric nebulizers have the benefits of excellent sensitivity and stability, but the small breakable fused silica holes are disposed to blockage, especially when aspirating samples of high salt content.
- Cross flow nebulizer is designed to reduce the clogging problem in contrast to concentric nebulizers, it use a high-speed stream of argon perpendicular to the tip of the sample capillary and broke sample solution into an aerosol with its drawbacks include lower sensitivity and potential capillary misalignment.
- Babington nebulizer that allows a film of the sample solution to flow over a smooth surface having a small hole high-speed argon gas coming from the hole shears the sheet of liquid into small droplets and the sample solution flows freely over a small aperture, rather than passing through a fine capillary, resulting in a high tolerance to dissolved solids and the least susceptible to clogging of very viscous liquids is its vital feature [30]

2.6.3 Spray chambers

A spray chamber is used to remove large droplets by means of gravity from the aerosol and to smooth out pulses produced by the peristaltic pump that may occur during nebulization. Thermally stabilized spray chambers are sometimes adopted to decrease the amount of liquid introduced

into the plasma, thus providing stability especially when organic solvents are involved and some ICP-OES spray chambers are externally cooled for thermal stability of the sample and to minimize the amount of solvent going into the plasma ^[47]. Using the one-dimensional continuity equation and Bernoulli's equation, we have

$$V_A A_A = V_B A_B \dots\dots\dots 16$$

and
$$\frac{P_A}{\rho} + \frac{1}{2} V_A^2 = \frac{P_B}{\rho} + \frac{1}{2} V_B^2 \dots\dots\dots 17$$

respectively and the pressure difference is

$$P_A - P_B = \frac{1}{2} \rho V_A^2 \left(\left(\frac{V_B}{V_A} \right)^2 - 1 \right) \dots\dots\dots 18$$

This is used to shear the water and form atomization by spray chamber ^[46].

2.6.4 Drains

The drains carry excess samples that can have impact on the performance of ICP-OES from spray chamber to waste container. Beside this, it provides back pressure used to force the aerosol through torch in to plasma discharge ^[40].

2.7 Source of Energy for ICP-OES

2.7.1 The ICP torch and its configurations

The plasma torch consists of three concentric tubes, which are usually made from quartz. These are the outer tube, middle tube, and sample injector.

- The argon gas used to form the plasma flows between the outer and intermediate quartz tubes.
- The auxiliary gas, between the middle tube and the sample injector

The nebulizer gas, carries the sample, in the form of a fine-droplet aerosol, from the nebulizer through the injector tube into the ICP torch that directs the sample through the center of the

plasma^[48]. There are two basic modes of torch configurations used to observe emission from the ICP. Plasma can be viewed as radial (side-on) and axial (end-on). The third viewing is merging the two basic modes together which commercially available is dual-view and each viewing has its own merit and disadvantage.

Radial viewing: The plasma in NAZ is observed from the side of the plasma but this viewing constrains the observation volume in the NAZ, and thus limits the effect of potential spectral and background interferences.

Axial viewing: The plasma is rotated to a horizontal position and the NAZ of the ICP is observed from the end of the plasma and it provides

- better LODs than radial view
- better sensitivity and Its shortcoming are
- the increased potential for spectral interference
- matrix -induced interferences.
- self-absorption

Dual viewing: used for very complex sample matrices having a wide range of elemental concentrations, and lets the user to optimize the suitable configuration for the type of sample without the expense of two separate configurations ^[32].

2.7.2 Radio Frequency (RF) generator and Load Coil

It is a device that provides the power required for the generation and sustaining of the plasma discharge. Its function is to deliver power required to obtain and maintain the plasma, portions of which are as hot as 10,000°K. This power, typically ranging from about 700 to 1500 watts is transferred to the plasma gas through a load coil surrounding the top of the torch. The coils are made of copper tubing and is cooled by water during operation. Any variation in the load that is in the type of solution inserted in the plasma is compensated for by a modification in the coupling between the primary lines and the lines of the secondary circuit. The frequency is selected at 40.68MHz, which is a high frequency thus providing a weak background and excellent limits of detection ^[49].

2.8 Interferences

Any chemical or physical process that dangerously distress the measurement of the radiation of interest is called as an interference. Interferences in ICP may start in the sample preparation phase and range to the plasma operating conditions. ICP and other methods of Spectrochemical analysis are typically subject to errors due to different types of interference:

- Physical interference due to changes in viscosity of the solution,
- Chemical interference due to the generation of compounds that have low atomization efficiency,
- Spectral interference due to the superposition of emission/ absorption lines, and
- Ionization interference which is a phenomenon that shows a change in emission intensity, causing the ionization equilibrium to shift, when coexisting elements include easily ionizable elements such as Na, K, Rb, and Cs.
- Non-spectroscopic interferences are characterized by the physical properties of the sample (e.g. viscosity), matrix composition, instrumental setup and operating conditions. Generally, this results in greater intensity of neutral lines and reduced intensity of ionic lines ^[41].

2.9 Emission Collector, Detector and Processor

2.9.1 Focusing system

The emission of radiation from NAZ of plasma is focused on the entrance slit of wavelength dispersive device or spectrometer. Collecting ions by focusing optics are critical for the whole sensitivity of the instrument, because scattered ions will not be detected. Ion focusing is achieved by subjecting the charged ions to constant electric fields. A secondary but also very important role of the ion optic system is to prevent particulates, neutral species and photons from entering to the mass analyzer and detector. These species cause signal instability and contribute to background levels, which ultimately affect the performance of the system ^[39].

2.9.2 Diffraction grating

The diffraction grating is always the core of the spectrometer and commonly used with most modern instruments to break down the white light into a number of different wavelengths. It is

simply a mirror (glass support) covered with a photosensitive layer with a large number of etched parallel lines (between 1800 and 4320 lines/mm). When light strikes such a grating, it is diffracted at an angle that is dependent on the wavelength of the light and the density of the grating ^[40].

$$m\lambda = d(\sin\theta_i - \sin\theta_r) \dots\dots\dots 19$$

Where Monochromatic beam incident on (blazed) diffraction grating at angle θ_i and diffracted at angle θ_r . The blaze spacing is d . and $m = 0, 1, \dots$, m is called the diffraction order. Grating is combined Spectrometer that form the light in to well ^[42].

2.9.3 Wavelength Dispersion Device.

Dispersion is the differentiation of emission radiation from one element from the radiation emitted by other elements or molecules and defined as

$$D = \frac{\Delta\theta}{\Delta\lambda} \dots\dots\dots 20$$

where D is angular dispersion and $\Delta\theta$ is the angular separation of two lines whose wave length differ by $\Delta\lambda$. It is possible to define angular dispersion as

$$D = \frac{m}{d \cos\theta} \dots\dots\dots 21$$

where d is the grating space and m is diffraction order ^[43].

The above equation confirms that when light strike a grating it is diffracted at an angle that depends on the wave length of light and the line density of the grating. To disperse polychromatic light confidently, the grating is combined with spectrometer that form the light into a distinct beam, disperse it according to wavelength with a grating, and focus the dispersed light onto an exit plane or circle ^[53]. In order to measure several elements from the same sample the two commonly used devices in ICP are Polychromator and Monochromator.

- Polychromator is device with multiple exit slits and detectors in the same spectrometer, each exit slit is aligned to an atomic or ionic emission line for a specific element to allow simultaneous multi element analyses.

- Monochromator has only one exit slit and detector and used in multi element analyses by scanning rapidly, or slewing, from one emission line to another with sufficient speed rapid sequential multi element analyses are possible. Either by changing the angle of the diffraction grating by rotating it or by moving the detector in the exit plane of the monochromator while leaving the grating in a fixed position this means a sequential (monochromator) device usually comprises an input slit controlled by computer through which the light emitted from the plasma enters; a collimating mirror which sends light to the grating used for light diffraction; and a mirror which transmits light to the output slit [43].

The resolving ability of a monochromator refers to its power to separate adjacent wavelengths, represented mathematically by

$$R = \frac{\lambda}{\Delta\lambda} \dots\dots\dots 22$$

where;

R is resolving power, λ is wave length, $\Delta\lambda$ wave length difference of consecutives waves [38].

2.9.4 Detector, Computer and Processor

Detectors: Once the proper emission line has been isolated by the spectrometer, the detector and its associated electronics are used to measure the intensity of the emission line by using modern, advanced detector systems based on charge transfer technology in silicon wafers.

Signal Processing: At the time advanced detectors picture of a wavelength region, all of the intensities within this region are converted into digital information and may be permanently stored.

Computers and Processors: The computer controls incorporated into the instrument to run every ICP-OES instrument. The majority of automated functions of an ICP-OES instrument are directly controlled by an on-board computer through button or a keypad located on the instrument. However, an external computer, interfaced to the instrument's on-board computer, acts as an interface between the analyst and the instrument. Despite the fact almost every commercial ICP-

OES instrument available today uses some type of computer to control the spectrometer and to collect, manipulate, and report analytical data, the amount of computer control over other functions of the instrument varies widely from model to model ^[33]. In the most sophisticated ICP-OES instruments:

- Calibration
- Sample introduction
- Plasma formation
- Condensing emission from NAZ
- Identification of wavelength via differentiating in the Spectrometer
- Detecting intensity
- Converting signal in to digital and other functions of the instrument under the

control of the computer (automated) ^[40].

UNIT THREE

3. Materials and Methods

3.1. Description of the study area

The study area is located about 195 km east of Addis Ababa, in Oromiya Regional State, Shoa Zone, in the district of Metehara. It is within the Main Ethiopian Rift (MER) in the Awash basin. The study area is crossed by one main asphalted road and the Addis Ababa Djibouti rail way line. The samples were taken from four reachable sides of lake Beseka and one sample of Beseka water is taken from the initial part of the drainage canal located at east of north of Beseka Lake. Then two samples were taken from upstream around Merti bridge and three samples were taken from downstream at distances far away from the mixing point of Awash River and Beseka water, which is located at south east Lake Beseka

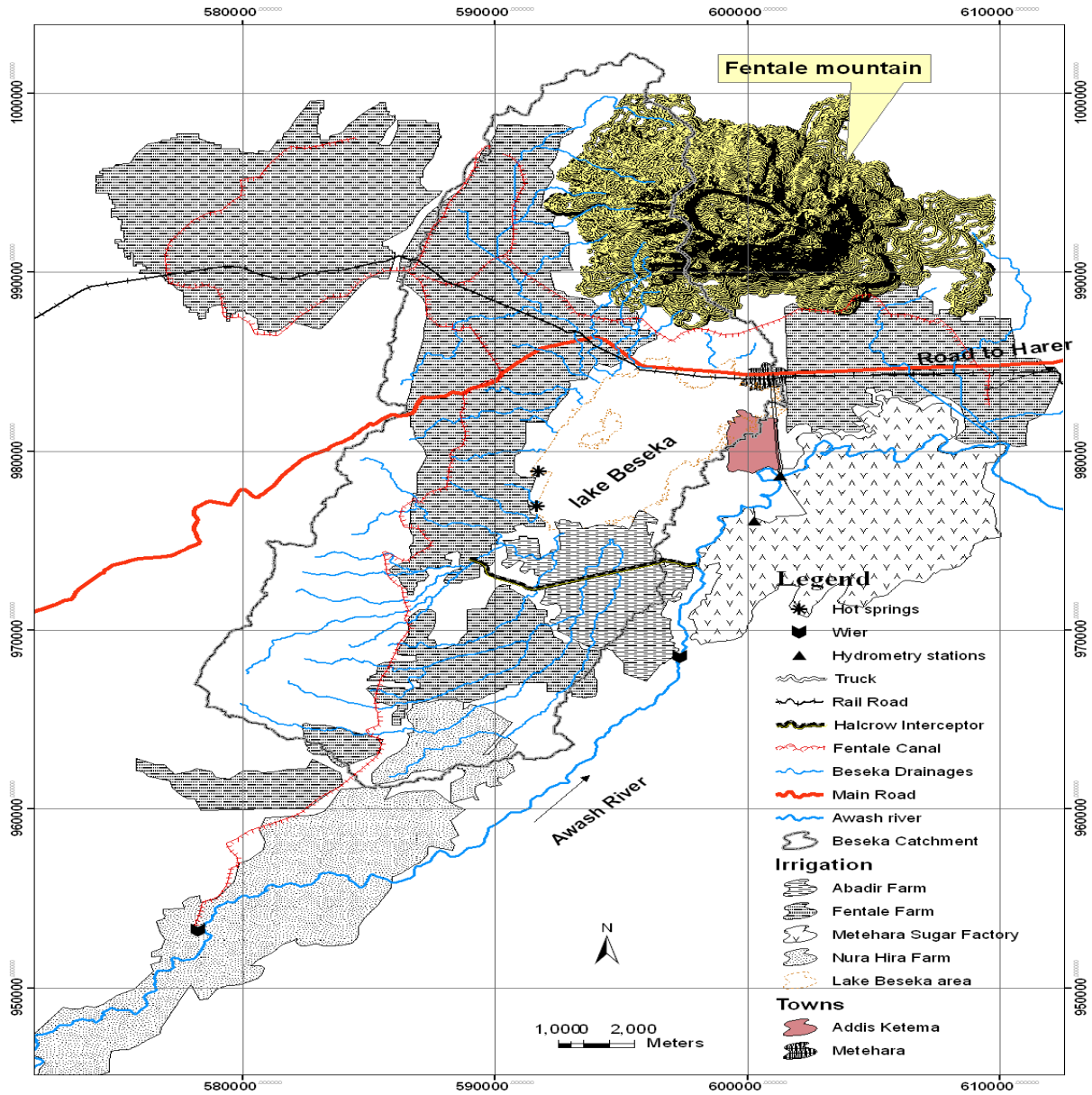


Figure3.1. Location of the study area: Location map and drainage network of the watershed
(Source:Water Works Design and Supervision Enterprise)

3.2 Sampling

Sampling is the process of selecting a group of subjects for a study in such a way that the individuals represent the larger group from which they were selected. The study were aimed at conducting systematic investigations on the chemical analysis of water of Lake Beseka. Systematic random approach will be employed. Five Samples of water were taken from all sides of the lake and five samples of water of Awash river will be taken from the upper and lower part of the gate of entrance of Beseka 's water into the river. At the downstream of the river, one sample was taken from Awash 7kilo town and the other two samples were taken with distance of 500 meters each from the entrance of the discharged water of Lake Beseka. And again two samples of water were taken from the upper stream of the river 1 up to 2km's away from the gate of entrance Beseka water into the river. Finally, one sample was taken from the canal in which Beseka 's water is let to Awash river and the other four samples were taken from four sides of Lake Beseka in order to get an average value of the concentration of contaminants. It is also advantageous from statistical point of view that it will raise the number of samples required with the amount of unfairness introduced by sample selection, sampling, storage or analysis. In other words, with relatively small number of samples, a wide amount of bias will be introduced. At last it helps to picture the current analysis of water of Lake Beseka and observe the extent of its contribution to the pollution of Awash River.

3.3. Apparatuses needed to the study

Experimental equipment needed to study the water samples are:

- ❖ pH meter to measure acidity and alkalinity conductometer
- ❖ to measure conductivity
- ❖ test tubes of 15c.c. and glass cubit for sample preparation and introduction
- ❖ a photo spectrometer (which applies ICP-OES) to measure the kind and concentration of chemical elements and compounds as well as the turbidity.
- ❖ MS office xl program soft wear to prepare analytical graphs.

3.4. The sources of data

Data sources that will be used in the study are both primary and secondary ones. The Primary data will be collected from the water of Beseka Lake and Awash River; secondary data will be collected from recent publications, relevant books, journal and relevant technical document and the third data will be collected from them computer output data of the given water samples.

3.5. Transport and Pretreatment Sample preservations

The water samples will be collected in carefully cleaned bottles and just transported to laboratory. After Samples are carefully filtered through Whitman filter papers it will be transferred into 15ml volumetric flasks and be stored in a refrigerator until they are analyzed.

3.6. Sample introduction

Water is transport form container by peristaltic pump to nebulizer which changes water in to an aerosol. Then after spray chamber remove large aerosols by use of gravity and only an aerosols of fine droplet introduced to central part of ICP-OES. While entering the plasma the fine droplet of water passes three steps, namely desolvation, vaporization and atomization. Before leaving the plasma and entering the next instrument atoms are excited and ionized with available energy in ICP which promoted them to their respective excited states and both relax to ground via emission of photon that have characteristic energies determined by the quantized energy level structure for the atoms or ions. The total number of photons is directly proportional to the concentration of the originating element in the sample. A portion of the photons emitted by the ICP is collected with a lens or a concave mirror and forms an image of the ICP on the entrance aperture of a wavelength (identify the elements from which they originated) selection device called a monochromator. The particular wavelength exiting the device is converted to an electrical signal by a photo detector. The signal is amplified and processed by the detector electronics, then displayed and stored by a personal computer.

UNIT FOUR

4. Data analysis

4.1. Data collection summary

Ten samples of water were collected from five different parts of Lake Beseka and five samples were collected from Awash River, among them two samples were collected from the upper part of the river before it joins the outlet of the canal which brings Beseka's water into it and the other three samples from the lower part of Beseka's outlet. The samples coded with later A and B for water samples from Awash River and for water samples from Lake Beseka respectively. These samples were collected with properly cleaned plastic bottles of 1&1/2 liter. The overall data collected from each samples of water is tabulated bellow in tables 4.1, 4.2, 4.3, & 4.4.

No	Samples code	Location of the samples taken
1	A ₁	From Awash river at Awash Town
2	A ₂	From Awash River under the Merti Bridge
3	A ₃	1km away from the point where sample A ₂ was taken
4	A ₄	1km away from the point at which Beseka's water meets with Awash River
5	A ₅	500 meters away from the meeting point of Awash River and Beseka's water.

Table 4.1. Location of samples taken from Awash River

No	Samples code	Location of the samples were taken
1	B ₁	At initial point of the canal that transports Beseka's water.
2	B ₂	East of north side of Lake Beseka
3	B ₃	From right side of the older rail way
4	B ₄	In between the older rail way and older asphalt road
5	B ₅	From the left side of the older asphalt road

Table 4 .2. Location of the samples collected from Lake Beseka

4.2. Laboratory procedures

- ✚ All the test tubes were prepared
- ✚ All equipment was placed on their proper place
- ✚ Distilled water is prepared using distillation machine
- ✚ Sample of a distilled water of 10mm³ is taken by a glass cubet as reference of measurement.
- ✚ First the conductivity and pH value of each samples were taken and recorded
- ✚ Then the sample of distilled water was introduced to ICP-OES machine as reference for each measurement taken

The concentration of nine types of chemicals in each samples mixing nine kinds of reagents in 10mm³ water of a sample in each cells. The samples are then introduced to the ICP-OES machine. Then measurements of each parameter taken from its display screen by selecting the parameters to be measured using selecting button of the machine. Total of ninety measurements were taken for all ten samples of water in a similar way and all results were recorded.



Figure 4.1 Clean test tubes and apparatuses prepared for sample tests



Figure 4.2. An apparatus used to prepare distilled water.



Figure 4.3. Water samples prepared for measurement.

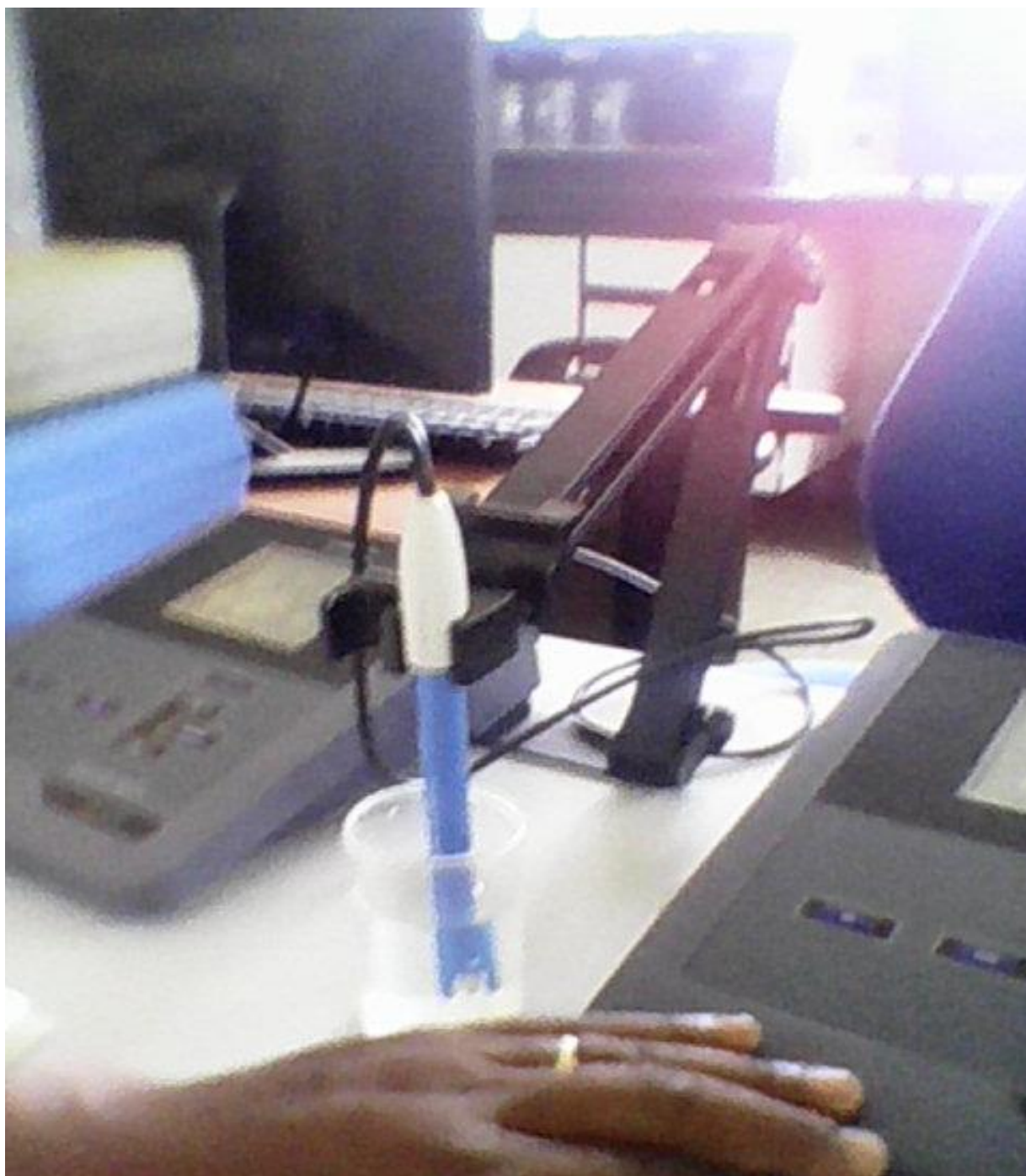


Figure 4.4. Conductometer and p H meter to measure conductivity and p H respectively.



Figure 4.5. An ICP-OES photo spectrometer

4.3. Data analysis, Result, and Discussion

No	Parameters measured	Units	Samples				
			A ₁	A ₂	A ₃	A ₄	A ₅
1	Conductivity	μS/cm	423	241	249	3270	3271
2	TDS	mg/l	240	135	139	1830	1848
3	pH		8.6	7.7	8.13	9.7	9.7
4	Iron(Fe)	mg/l	0.88	0.20	0.67	0.25	0.36
5	Fluoride(F)	mg/l	0.02	0.60	0.03	1.43	1.06
6	Aluminum (Al ⁺³)	mg/l	3.3	3.6	2.93	0.23	0.233
7	Chromium (Cr)	mg/l	0.646	0.216	0.524	0.276	0.308
8	Cyanide (Cn ⁻)	mg/l	0.138	0.038	0.113	0.053	0.061
9	Nitrate (NO ₃ ⁻)	mg/l	0.61	0.143	0.39	0.192	0.220
10	Sulfate (SO ₄ ²⁻)	mg/l	195	112	165	390	480
11	Ammonia NH ₄	mg/l	0.43	0.05	0.30	0.11	0.16

Table4 .3. Experimental result found in the water samples from Awash River.

No	Parameters measured	Units	Samples				
			B ₁	B ₂	B ₃	B ₄	B ₅
1	Conductivity	μS/cm	3470	3084	3450	1560	4300
2	TDS	mg/l	1925	1728	1928	875	2150
3	pH		9.7	9.8	9.7	9.7	9.8
4	Iron(Fe)	mg/l	0.10	0.17	0.03	0.08	0.07
5	Fluoride(F)	mg/l	16.2	19.6	17.4	17.52	24.16
6	Aluminum (Al ⁺³)	mg/l	0.210	0.260	0.354	0.246	0.191
7	Chromium (Cr)	mg/l	0.160	0.179	0.142	0.118	0.123
8	Cyanide (Cn ⁻)	mg/l	0.030	0.033	0.022	0.019	0.014
9	Nitrate (NO ₃ ⁻)	mg/l	0.025	0.080	0.006	0.037	0.035
10	Sulfate (SO ₄ ²⁻)	mg/l	380	108	440	384	90
11	Ammonia NH ₄	mg/l	—	0.05	—	—	—

Table 4.4. Experimental result found in samples taken from Lake Beseka

4.3.1. Analysis of physical parameters

In studying the property of water in lakes and rivers the physical parameters observed are the pH values, TDS, conductivity, and turbidity. Among these the pH and the conductivity of the given samples are investigated as follows.

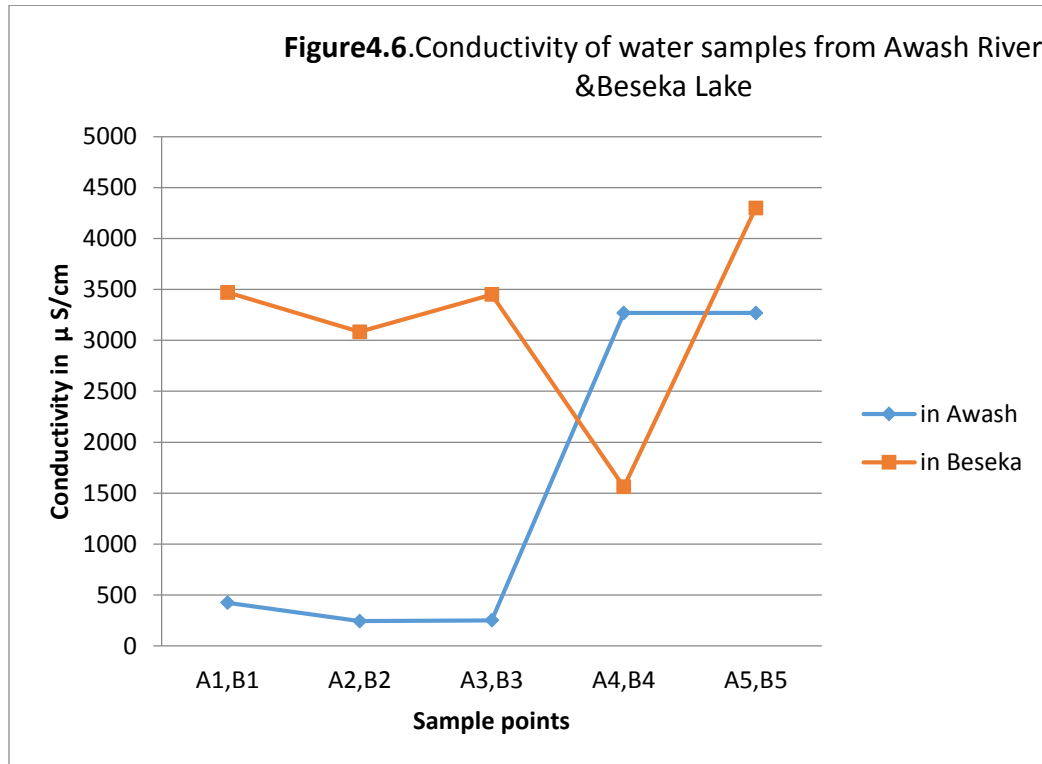


Figure 4.7 shows that the conductivity is found to be higher at points A4 and A5, which are located very nearer to the outlet of the Beseka's canal. At point A2 and A4, which are located a few kilometers away from the outlet of the canal in the upstream of the Awash River, the result shows the conductivity is very smaller than the value after the river water is mixed with Beseka's water. And at A1, which is about 15km of downstream from the outlet of the drainage canal. It also shows that the conductivity at points B1, B2, and B3 are almost constant and it increased at point B5, which is located to left side of the older asphalt road from Addis Ababa and it is the nearest location of Beseka to the Mountain of Fentale. But the conductivity of the sample water at point B4 is very small compared to that of point B5. This is because it is a point of interance of runoff water coming from Metahara Town and mix with Beseka Lake. It was rainy one day before the samples were taken.

The variability of the amount of conductivity in the water samples of Awash River is mainly due to the concentration of ions decreases as it goes far away from the mixing point with Beseka's discharged water. Conductivity in water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulphate and phosphate ions or sodium, magnesium, calcium, iron and aluminum ions, it is also affected by temperature ^[54]. According to WHO standards of water for drinking, the maximum allowable level of conductivity should be 500 μ S/cm. Even though the magnitude of conductivity decreases as we go far away from Beseka's entrance, as the results shown in figure 4.7; the quality of water for irrigation as well as for drinking in the area nearer to the mixing point, are in danger. The measured conductivities exceed high in the vicinity of the mixing point of the lake.

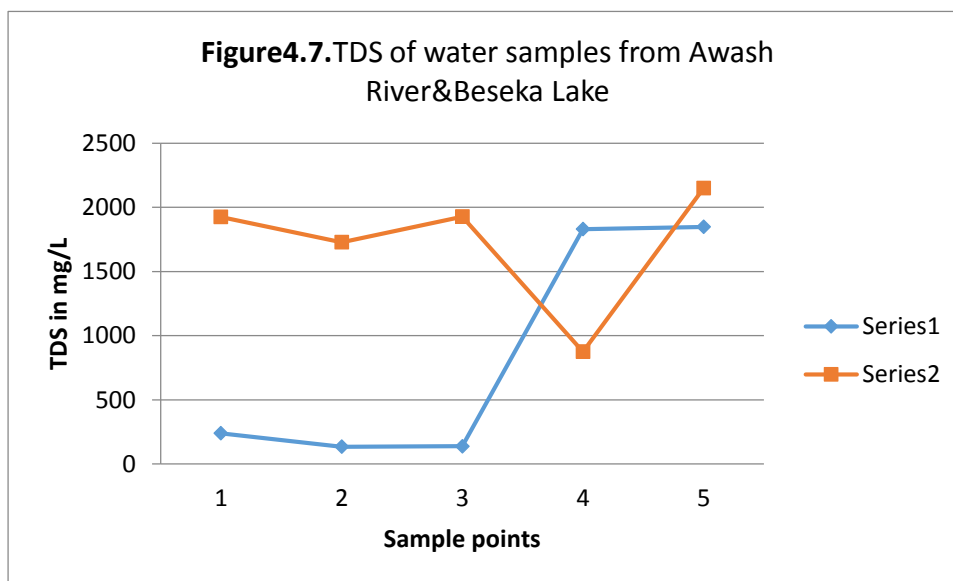


Figure 4.8. shows the TDS of the river's water is highly affected at a distance nearer to the mixing point of Beseka's. The

TDS of the river around the mixing point exceeds the WHO standard limit of TDS for drinking water, which is 1,000ppm. But it is less at a long distance away from the mixing point. The dissolved salts of calcium and magnesium such as bicarbonates, chlorides and sulphates are responsible for causing the hardness in the water.

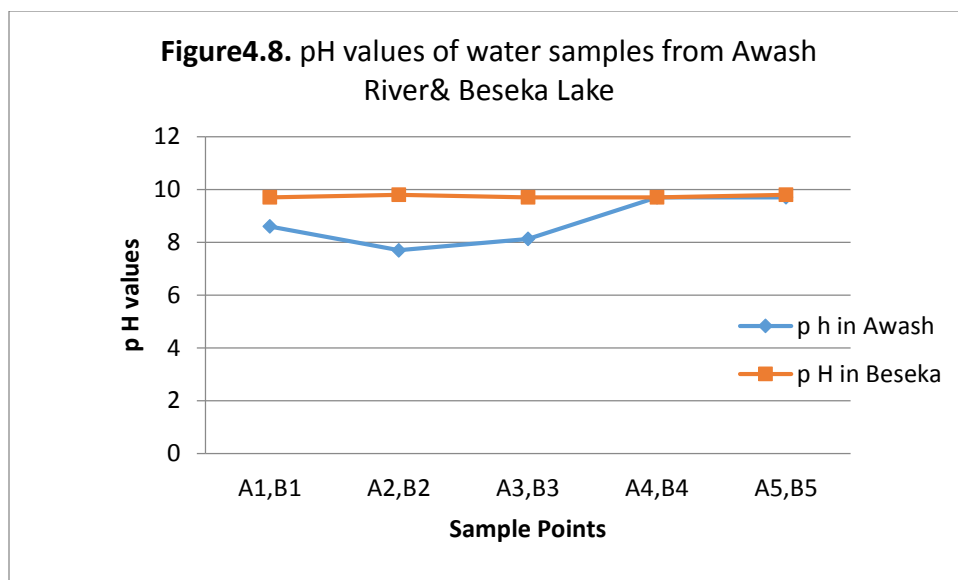


Figure 4.9. shows that the pH of water samples of Awash River nearer to the lower part of the junction of Beseka 's discharge water is nearly equal. The sample that was taken at Awash 7kilo town is 8.6. According to WHO standards pH of drinking water should be 6.5 to 8.5 and the water from Awash River at this town exceeds WHO's standard. The average pH of Beseka Lake is about 9.74. It exceeds the given standard and these is not potable water for human as well as animal's. But it is somewhat harmless for fishes. There is no normal pH that applies to all fishes. This also shows that because fish originate in ponds, rivers, lakes, oceans that have different pH levels. But sudden change of pH can be harmful or even fatal to fishes. In the dry season the dissolved oxygen level becomes very low and the river becomes very toxic to aquatic animals ^[55]. Variations in pH values are mainly due to hydrolysis of salts of strong bases and weak acids or vice versa. Dissolved gases such as carbon dioxide, Hydrogen sulphide, ammonia etc also affect the pH of the water ^[44].

4.3.2. Analysis of chemical parameters

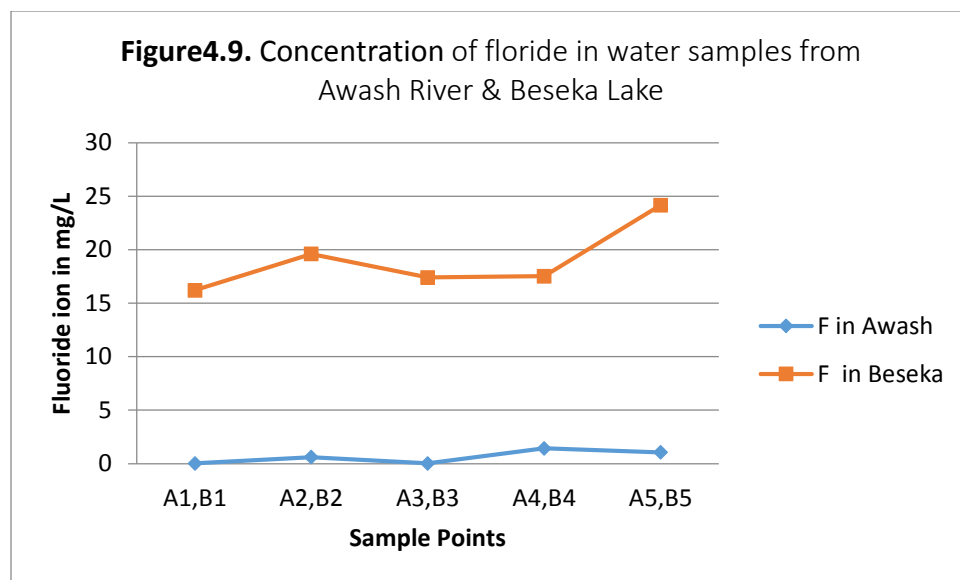


Figure 4.10. shows that the fluoride content of Awash River and Beseka Lake based on the results found from the samples taken. The fluoride content of the river's water samples taken at points A4 and A5 (i.e. which are nearer to the mixing point of the drainage canal of Beseka's water in the direction of the downstream) shows higher concentration than the samples of the river water taken away from the outlet of the drainage canal (A2, A3) have lower fluoride concentration. The least concentration was measured in the sample taken at about 17km downstream from the drainage canal. This result also implies that the concentration of the fluoride content of the river is affected highly around the outlet of the Beseka Lake and is decreasing as the river moves away far from the drainage canal. In general, the average value of the fluoride of Awash River in the range of 1km is about 1.245mg/L which is nearer to the WHO's standard for the maximum value of fluoride in drinking water (i.e. 1.5mg/L). At concentrations greater than 1.5mg/L, fluorosis (mottling) of teeth may occur. At concentration below 1.0mg/L dental cavity can occur on the teeth. In case of plants growth, up to 120mg/L fluoride of irrigation water did not harm the plants [45].

In addition, figure 4.10. shows the concentration of the fluoride of Beseka Lake ranges between 16 & 25mg/L. The average value of fluoride in taken samples is about 19.064mg/L. It exceeds WHO's standard. Unless some measures are taken on the lake's water it cannot be useful for drinking purpose.

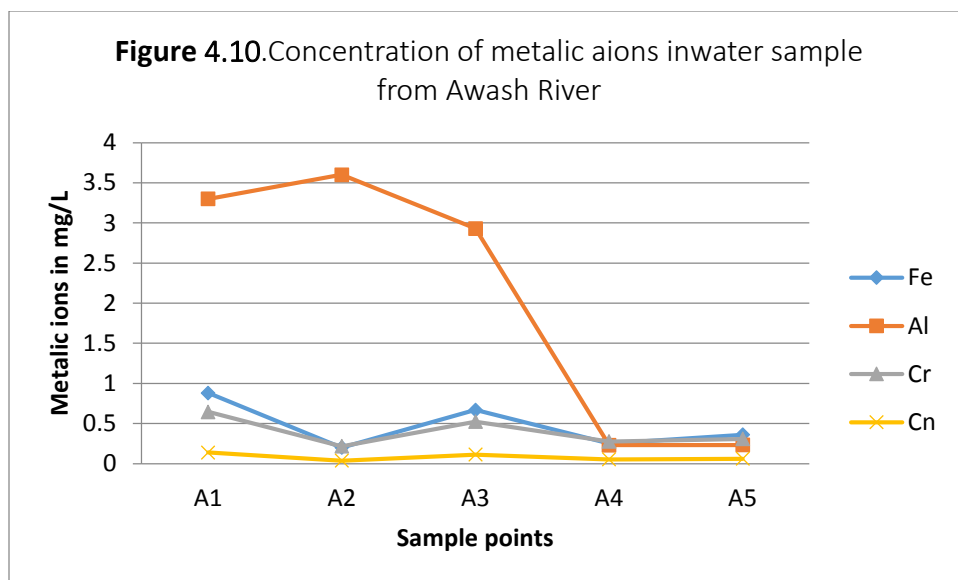


Figure 4.11. shows that the concentration of aluminum ion is the greatest of the other three metallic ions investigated. Its magnitude is greater at sample points A1, A2, and A3. Its concentration becomes lower at points down stream of the mixing point of Beseka 's drainage canal and is increasing as we go far away on both the upstream and downstream of the river from the outlet of the drainage canal. The same thing happens in the concentration of Cr, Fe, & Cn. Concentrations of aluminum at which such problems may occur are highly dependent on a number of water quality parameters and operational factors at the water treatment plant. Acid environments caused by acid mine drainage or acid rain can cause an increase in the dissolved aluminum content of the surrounding waters ^[46]. Based on the pH data collected, the water samples from above and below the outlet of the drainage canal is weak alkaline. this contributes a bit to the increasing of aluminum ions. The concentration of aluminum in natural waters can vary significantly depending on various physicochemical and mineralogical factors. Dissolved aluminum concentrations in waters with near-neutral pH values usually range from 0.001 to 0.05 mg/liter but rise to 0.5–1mg/liter in more acidic waters or water rich in organic matter. At the extreme acidity of waters affected by acid mine drainage, dissolved aluminum concentrations of up to 90mg/liter have been measured (WHO, 1997). Aluminum levels in drinking-water vary according to the levels found in the source water and whether aluminum coagulants are used during water treatment. In Germany,

levels of aluminum in public water supplies averaged 0.01 mg/liter in the western region, where as levels in 2.7% of public supplies in the eastern region exceeded 0.2 mg/liter^[46].

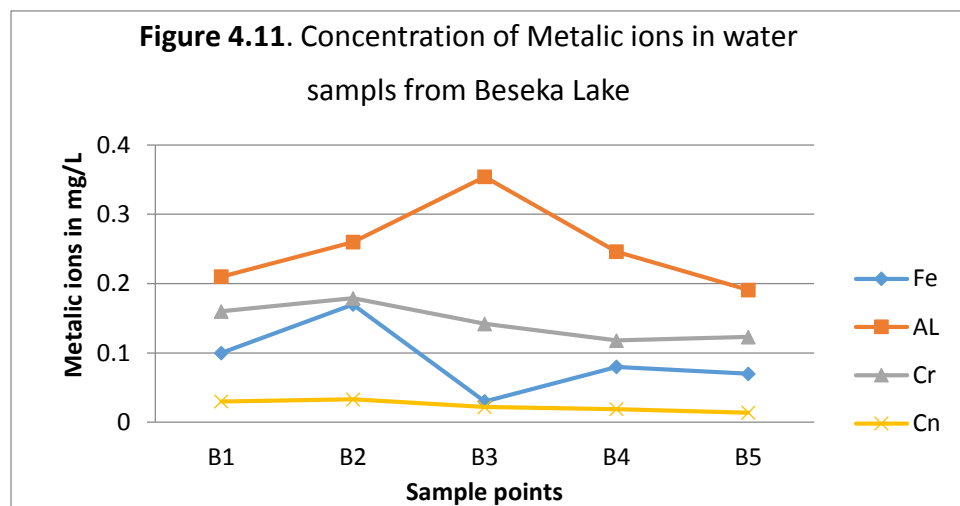


Figure 4.12. Like in that of the Awash River the concentration of aluminum ions is the greatest of all the other three metallic ions found in the water samples from Beseka Lake. It ranges between 0.191 up to 0.354mg/L. Likewise, the level of presence of these metallic ions can be written as: the concentration of $Cr > Fe > Cn$, respectively. Their level of concentration is more in Bseka Lake than their concentration in Awash River. This condition makes Beseka to be a saline lake with additive factors of the others metallic ions which were not investigated in this study due to the problems mentioned above.

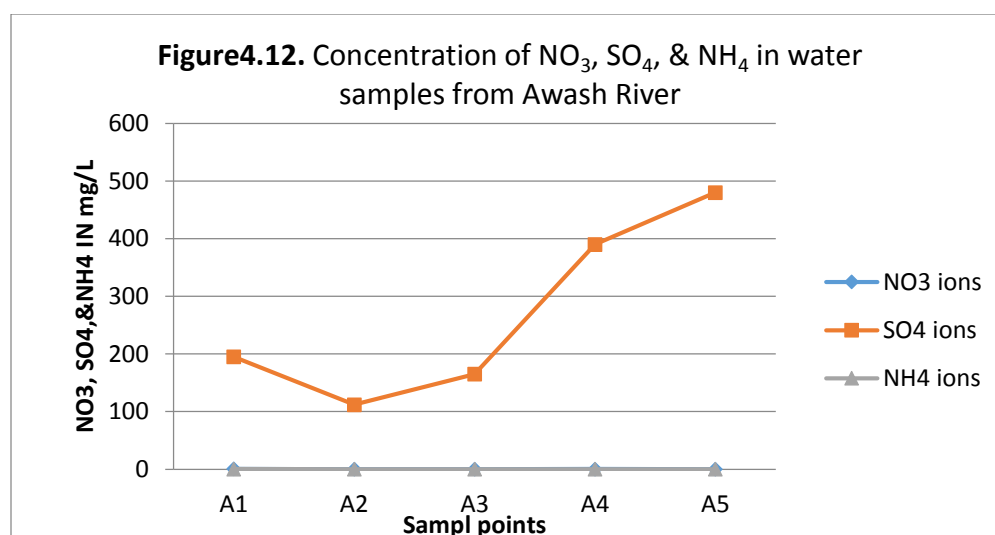


Figure 4.13. shows the concentration level of NO_3 , SO_4 , and NH_4 in samples from Awash River. The result found shows that the concentration of the sulfate ion is greater than ammonia and nitrate ions. Here, in chart 6 the magnitude of sulfate's ion concentration is recorded at sample points of A5, A4, & A3, descending respectively. These points are located in the downstream of the river which is at the lower part of the mixing point with Beseka's discharged water. The value of the average concentration of nitrate in samples from Awash River is 0.311mg/L and 268.4 mg/L for sulfate and 0.21mg/L for ammonia.

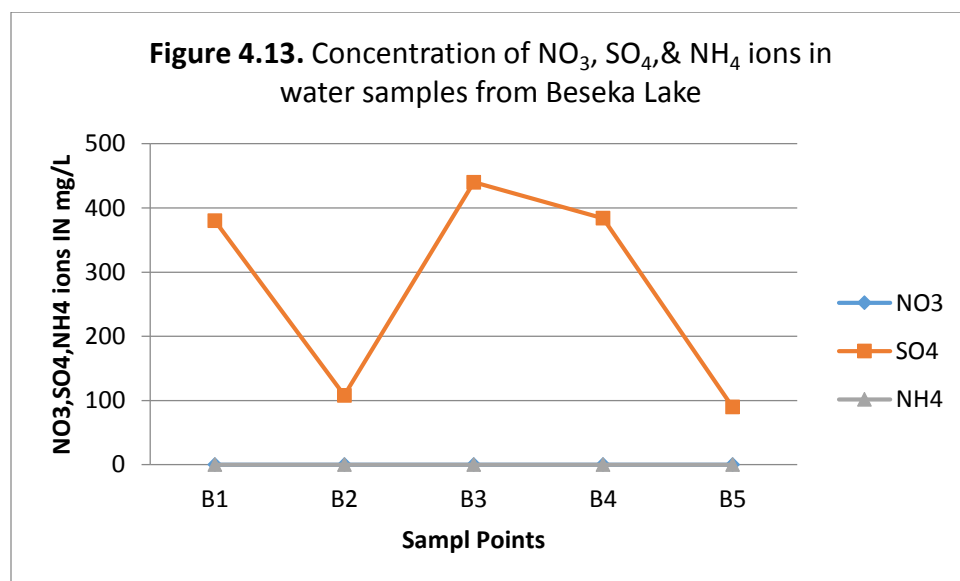


Figure 4.14. shows the concentration of nitrates, sulfate, & ammonia ions water samples taken from Beseka Lake. The magnitude of sulfate is the greatest all other ions investigated and its average value is of 280.4mg/L. Ammonia shows the smallest concentration of the other ions. It is almost null. But the concentration of ammonia ranges between 0.006mg/L up to 0.08mg/L with an average value of 0.0366mg/L. The maximum allowable concentration of nitrate in drinking water and the side effect of the intake of nitrate beyond this level is mentioned in section 2.3.7. Nitrogen, like phosphate, is essential to plants and animals for proper growth and productivity. The air we breathe is composed mainly of nitrogen gas (N_2). However, this form is impossible for aquatic plants to use. Therefore, most plants rely on bacteria, which "fix" or convert the nitrogen gas found in the atmosphere to a form called nitrate. Nitrate is present as an ion, or charged species in water. The nitrate ion is composed of a single nitrogen atom and three oxygen atoms (NO_3). Nitrate forms the important materials necessary for life, such as proteins and vitamins. When

animals digest these proteins they are converted to ammonia (NH_3). Ammonia in high concentrations in the body is toxic. All organisms, including fish, must get rid of ammonia through excretion. Ammonia is also produced when plants and animals decay. Two kinds of bacteria work in sequence to transform ammonia into nitrate. Ammonium oxidizers convert ammonia to nitrite, and nitrifying bacteria convert nitrite to nitrate. Both types of bacteria require oxygen to perform these reactions. Algae also help recycle nitrogen by converting ammonia into plant material. Harmful concentrations of ammonia hardly ever build up in natural waters due to recycling by algae and bacteria. The presence of ammonia is almost zero in sample from Beseka Lake. This is because there are no nitrifying bacteria within due to its alkaline property of the water.

UNIT FIVE

5. Conclusion and Recommendation

5.1. Conclusion

Among the twenty parameters that are proposed to be find out, eleven parameters of the ten water samples from Awash River and Beseka Lake were investigated using p H meter, conduct meter, and ICP-OES photospectrometer. Based on the experimental data, data analysis, and discussion the following conclusions are drawn. These are:

- ✓ It is found that Beseka Lake is more alkaline than Awash River. It has an exceeding value of p H permitted for drinking by WHO. It should be not used for drinking.
- ✓ The water of Awash River around the outlet of the drainage canal of Beseka's water is becoming light basic, which is caused by the mixing of the lake's highly conductive and TDS leveled water into it.
- ✓ It is observed that the concentration of Aluminum ion is greater in Awash River than its concentration in Beseka Lake. This is because, in pure water, Aluminum has a minimum solubility in the pH range 5.5–6.0; concentrations of total dissolved Aluminum increase at higher and lower pH values ^[45]
- ✓ Unlike to the concentration of aluminum, the concentration of sulfate is greater in Lake Beseka than it is in Awash River. This causes Beseka's water to smell unpleasant than the water from Awash River.
- ✓ The level of conductivity and TDS are greater in magnitude in the beseka water than in Awash River. It is observed that the level of conduction and TDS of Awash River are almost the same to that of Beseka's water around the vicinity of the out let of the drainage canal. This causes to increase the salinity of the River's water. And as a result some of the insoluble salts of heavy metals start to deposited along the river side's and affect the content of the soil in that area, which in the long run covers large area of salty soil that is not comfortable for plants growth.
- ✓ The fluoride content of Beseka Lake is extremely higher than it is in Awash River. To some extent the fluoride content in Awash flowing down around the end of the drainage canal is increasing a bit higher compared to in that of the water at far upstream and far downstream.
- ✓ It also found that both the River water and the Lake water have got small concentration of iron, cyanide, chromium, nitrate, and ammonia ions.

5.2. Recommendations

This study has tried to find out the chemical contents of Lake Beseka and its impacts on the water dynamics of Awash's River due to the immediate measure that has been taken to let it enter the river that obeyed by its expansion. The study area is wide with its large and complicated number of problems which cannot be covered by this study. The following recommendations are suggested as:

- Further studies should be taken place to find out the exact reliable contents of chemicals that covers all parts of the surface of Beseka's water. Studies also should be taken place how could some species of fishes and crocodiles exist in it.
- Make a big dame of soil and stones around the lake in order to arrest its expansion.
- Investigate further about the water dynamics of the river starting from its starting point up to its end to Lake Abe.
- Find out every scientific mechanisms of water treatment to make Beseka 's water suitable for drinking and for irrigation rather than releasing it to the river, which is the very useful source of drinking water for population of human and animals leaving on the sides of the river banks.
- Apply ICP-OES portable photo spectrometer in order to monitor the water quality every day in every district water treatment plants in order to find out the physical and chemical properties of dirking water any time and make a confidential decision in making a good proportion of additive chemicals which are mixed as a water treatment. The photo spectrometer is of model DR-1900 and it can detect about 55 chemicals in the water samples.
- Find scientific mechanism of extraction of salty substances in the Beseka Lake and reduce its salinity and alkalinity of in orderfore its water used for irrigation purposes rather than discharging it in to the river.

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