Assessment of Physico-chemical Characteristics and the Level of Selected Trace Metals in Spring Waters of Hericha Kebele, Haru District, West Wollega Zone, Oromia Region, Ethiopia

By
Solomon Yadesa

Applied Chemistry Department

School of Applied Natural Science

In Partial Fulfillment of the Requirements for the Degree of

Master of Science in Chemistry

Adama Science and Technology University

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September, 2017

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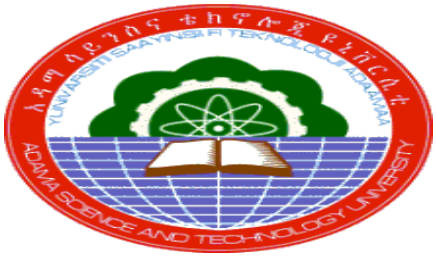

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Approval of Board of Examiners

We, the under signed, members of the Board of Examiners of the final open defense by Solomon Yadesa have read and evaluated his/her thesis entitled **"Assessment of Physico-chemical Characteristics and the Level of Selected Trace Metals in Spring Waters of Hericha Kebele,Haru District,West Wollega Zone, Oromia Region, Ethiopia"** and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

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DECLARATION

I hereby declare that this MSc Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

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The superior Lord Jesus Christ may bless all of you throughout your life.

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ABREVIATIONS AND ACRONYMS

AAFRD	Alberta Agriculture, Food and Rural Development
AAS	Atomic absorption spectrophotometer
CCS	Continuing calibration standard
COD	Chemical oxygen demand
EBT	Eriochrome black-T
EC	Electrical conductivity
EDTA	Ethylene diamine tetra acetic acid
EEPA	Ethiopian environmental protection authority
FAAS	Flame atomic absorption Spectrophotometry
FAS	Ferrous ammonium sulfate
IDL	Instrument detection limit
LFB	Laboratory fortified blank
LFM	Laboratory fortified matrix
LRB	Laboratory reagent blank
MCL	Maximum contaminant level
MDL	Method detection limit
TA	Total alkalinity
TDS	Total dissolved solids
TEC	Threshold effect concentration
TH	Total hardness
TSAWQG	Tentative South African water quality guidelines
UNEP	United nations environment programme
USDA	United states department of agriculture
USEPA	United states environmental protection agency
WHO	World health organization

ABSTRACT

The present study was undertaken to assess the spring water quality in Hericha rural area of Haru district, West Wollega, Oromia, Ethiopia. Spring water samples were collected from 4 spring sites, namely: Abba Fasige, Mumme, Abba Nura, and Chirecha. All the samples were analyzed for seven physico-chemical parameters (temperature, pH, total dissolved solids, chemical oxygen demand, conductivity, alkalinity, hardness, SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-, Ca, Mg, Na and K), and for six heavy metals (Mn, Cd, Cu, Cr, Fe and Zn) using standard methods. Temperature, pH and conductivity were measured in-situ. The COD, alkalinity, hardness, $^-$, Cl^-, Ca and Mg were determined by classical methods. SO_4^{2-}, PO_4^{3-}, NO_3^-, Na, K and heavy metals were analyzed by instrumental methods .The in-situ measurements showed that mean values of temperature, pH, and conductivity were ranged from 23.333 to 24.233^oC, 5.96 to 7.28, and 56.67 to 107.67 µS/cm, respectively. The mean results for TDS, COD, alkalinity, and hardness were varied from 38.67 to 71.33 mg/L, 8.67 to 10.67 mg/L, 22.67 to 38.67 mg/L, and 24.96 to 49.92 mg/L, respectively. The major chemical analysis showed that the mean values ranged from 3.24 to 5.59 mg/L for SO_4^{2-}, 0.07 to 0.34 mg/L for PO_4^{3-}, 1.26 to 32.6 mg/L for NO_3^-, 3.916 to 6.77 mg/L for Cl^-, 4.71 to 10.26 mg/L for Ca, 3,16 to 5.82 for Mg, 2.90 to 4.94 mg/L for Na and 0.79 to 2.33 mg/L for K. Among the six heavy metals analyzed for waters Cd and Cr were below the method detection limit. However, the concentration of Mn, Cu, Fe and Zn were ranged from mean values of 0.02 to 0.13 mg/L, 0.039 to 0.07 mg/L, 0.03 to 0.146 mg/L and 0.55 to 0.70 mg/L, respectively. The analyzed parameters in waters were below the currently recommended guidelines for drinking water quality except pH of three spring sites: Abba Fasige, Mumme and Abba Nura which were below in the range of WHO and different national water quality standard.

Key words: Classical methods, Heavy metals, Hericha, Instrumental methods

1. INTRODUCTION

1.1 Background of the Study

Water is the prime resource of man's food supply. But most important is the fact that water is a major constituent of all living matter, comprising up to two-thirds of the human body. Next to air we breathe, water is mankind's most important substance (Lawson, 2011). Freshwater is a finite resource, essential for agriculture, industry and even human existence. Without freshwater of adequate quantity and quality sustainable development is not possible (Ethiopian Water Technology Centre, 2008).

Water pollution is the contamination of water bodies (e.g. lakes, rivers, oceans, aquifers and ground water). This form of environmental degradation occurs when pollutants are directly or indirectly discharged in to water bodies without adequate treatment to remove harmful compounds.

In Ethiopia, the dominant source of drinking water used to supply major urban and rural communities is from wells and springs (Gebrekidan and Samuel, 2011). Although there are a few diversity of systematic and comprehensive water quality assessment programs in the country, there are increasing indications of water contamination problems in some parts of the country. The major causes of this contamination could be soil erosion, domestic waste from urban and rural areas and industrial wastes

The use of spring water sources for drinking and other domestic purposes is a common feature for many rural area communities in West Wollega zone. West Wollega zone is one of the western part of Oromia regional state. Hericha kebele one which found in Haru District at 4 km from Guyi town to the North, West Wollega zone, is a naturally gifted area with green forests and water resources which makes it favorable for agricultural activities such as mainly plantation of coffee, cultivation of different crops like teff, maize, sorghum, barley,andothers.

The common water sources in Hericha rural kebele community for drinking and other domestic uses is a naturally occurring springs. Many of these springs are road side springs which are susceptible to contamination from human and animal wastes. Regular monitoring of water quality parameters has been proposed by international organizations like WHO. It is important to assess these parameters in order to maintain the quality of drinking water. Many standards, both international and national, are available now. These standards recommend maximum permissible limits on several water quality parameters in order to avoid any adverse effect on the health of the population consuming the water. Therefore, this particular study focuses on the assessment of selected physico-chemical properties as well as some major and minor chemical constituents of spring waters in Hericha rural area communities in order to emphasize the quality of water based on the investigated parameters.

1.2 Statement of the Problem

Water has unique chemical properties due to its polarity and hydrogen bonds which means it is able to dissolve, absorb, adsorb or suspend many different compounds, thus, in nature, water is not pure as it acquires contaminants from its surrounding and those arising from humans and animals as well as other biological activities (WHO, 2007; McMurry and Fay, 2004). Thus, the great problem which initiates the researcher is that the Hericha kebele communities are using water of untested quality for drinking and other purposes.

The international water community continues to highlight good water quality as vital for securing the future of human and aquatic ecosystem health (UNEP, 2004). However, review of literature point out that no any water research study has been conducted regarding the quality of water in this area. This also might facilitate the researcher to conduct the study in this area from the point of view of water quality parameters.

1.3 Research Objectives

General Objective

❖ To determine the physico-chemical parameters as well as the selected trace metals of Abba Fasige, Mumme, Abba Nura and Chirecha spring waters .

Specific Objectives

- To determine selected physico-chemical properties (temperature, electrical conductivity, TDS, COD, pH, alkalinity, total hardness, Ca, Mg, Na, K, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) of the spring waters .
- To assess selected heavy metals (Mn, Cd, Cu, Cr, Fe and Zn) in the spring waters
- To compare the analyzed physico-chemical parameters and heavy metals among Abba Fasige, Mumme, Abba Nura and Chirecha spring waters
- To compare the results with the national and international standard of water quality for drinking.

1.4 Significance of the Study

This study is expected to give the baseline information about spring water quality for the public in Hericha peasant association regarding the selected physico-chemical and major chemical constituents, and as well as some heavy metals. Moreover, the study outcome will provides information about the acceptability of the waters for drinking by comparing with drinking water quality standards given by national and international agency.

2. LITERATURE REVIEW

2.1 Uses of water

The use of water includes drinking, washing and cleaning, transportation, providing hydroelectric power, irrigation and recreation. Living things need water to move nutrients in to their cells and to help them excrete wastes and toxins. Water is necessary in many chemical reactions and laboratory tests. Water is also necessary for many medical procedures, including dental treatments and dialysis(Residential End Uses of Water,2016). Clean water is an essential resource for drinking, irrigation, industry, transportation, fishing, support of biodiversity, and for absolute esthetic enjoyment. From ancient times, people have chosen to live near water; settling in river valleys, beside lakes, or along coastlines. For as long as humans have lived near waterways, they have also used them to wash away their wastes and pollute water bodies (UNEP/DFID, 2003; Chapman, 1996). When water becomes polluted, it loses its value economically and aesthetically, and can become a threat to human health, the survival of aquatic organisms and wildlife that depend on it (UNEP/DFID, 2003; ESA, 1998).

2.2 Water sources

In general there are two main types of water sources: surface water sources(lakes , seas , river, oceans, ponds etc) and ground water sources (springs , wells ,infiltration wells).

2.3 Spring Water

A spring or seep occurs when groundwater emerges naturally on the earth's surface by either gravity or artesian pressure. Springs have traditionally been used by allowing people and livestock direct access to the water and spring site. Springs commonly occur along hillsides and in low areas where porous soils or fractured rock formations allow water to flow onto the ground surface. Springs can occur at a single point or over a large area, called a seep. A slow hillside seep or trickle where no visible water flow is observed should not be considered a true spring. Springs are important sources of water to streams and other surface-water features. They also may be important cultural and aesthetic features. The constant source of water at springs leads to the abundant growth of plants, and many times to unique habitats for endemic species like spring snails (USDA, 2007; AAFRD, 2002; Virginia Water Resources Research Center, 1999).Water quality is important to consider before using a spring as a water supply. Water quality is defined in terms of the chemical, physical and biological

contents of water. Water quality guidelines provide basic scientific information about water quality parameters and ecologically relevant toxicological threshold values to protect specific water uses. Spring water is a system comprising both the main course and the tributaries, carrying the one-way flow of a significant load of matter in dissolved and particulate phases from both natural and anthropogenic sources. For this reason, most springs will need some treatment before thewater is considered safe for drinking. Testing helps to determine exactly how much treatment is necessary and may help to determine if other sources of water would be more economical(Geyikçi *et al.*, 2012; Lawson, 2011).

2.4 Physico-chemical Parameters

Physical and chemical properties are parameters that do not identify particular chemical species but are used as indicators of how water quality may affect water uses. These are temperature, electrical conductivity, total dissolved solids, chemical oxygen demandhydrogen ion concentration (measured as pH), alkalinity, and hardness (Weiner, 2008; USEPA, 2006).

2.4.1 Temperature

Temperature is an important biologically significant factor, which plays an important role in the metabolic activities of the organism. An increase in temperature changes the physical environment in terms of reduction in oxygen concentration of water bodies while increasing the metabolism of species such as fish that are very sensitive to changes in temperature (Harrison; 1990). Cool water is generally more palatable than warm water, and temperature will have an impact on the acceptability of a number of other inorganic constituents and chemical contaminants that may affect taste. High water temperature enhances the growth of microorganisms and may increase problems related to taste, odor, color and corrosion (WHO, 2011; Gopalkrushna, 2011).

2.4.2 Electrical Conductivity

Electrical conductivity (EC) is the measure of the ability of water to conduct an electric current and depends upon the number of ions or charged particles in the water. EC determinations are useful in aquatic studies because they provide a direct measurement of dissolved ionic matter in the water. Low values are characteristic of high-quality, low-nutrient waters. High values of conductance can be indicative of salinity problems but also

are observed in eutrophic waterways where plant nutrients (fertilizer) are in greater abundance. Very high values are good indicators of possible polluted sites. Conductivity often is used to estimate the amount of TDS rather than measuring each dissolved constituent separately (Government of Western Australia, 2009; Ethiopian Water Technology Centre, 2008; Alberta Environment, 2000).

2.4.3 Total Dissolved Solids

The term total dissolved solid (TDS) refer to materials that are completely dissolved in water (WHO, 2011, Ethiopian Water Technology Centre, 2008). Determination of the "solids" content is important for both aesthetic and practical reasons; drinking water with high solids content can have a disagreeable palatability. The palatability of water with a TDS level of less than about 600 mg/L is generally considered to be good; drinking-water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/L. Dissolved solids in natural waters may consist of carbonates, bicarbonates, chlorides, sulfates, phosphates, nitrates, magnesium, sodium, iron, manganese and other substances. Taste problems in water often arise from the presence of high TDS levels with certain metals present, particularly iron, copper, manganese, and zinc (Pradhan and Pirasteh, 2011; WHO, 2011; Weiner, 2008). TDS in water originate from natural sources, sewage, urban runoff, and industrial wastewater. Concentrations of TDS in water vary considerably in different geological regions owing to differences in the solubilities of minerals and the presence of high levels of TDS in drinking water may be objectionable (WHO, 2004).

2.4.4 Chemical Oxygen Demand

Chemical oxygen demand (COD) refers to the amount of oxygen consumed when all the organic matter in a given volume of water is chemically oxidized to CO_2 and H_2O by a strong chemical oxidant, such as permanganate or dichromate. COD is sometimes used as a measure of general pollution. For example, in an industrial area built on fill dirt, COD in the groundwater might be used as an indicator of organic materials leached from the fill material. Leachate from landfills often has high levels of COD. The COD analysis oxidizes organic matter that is both chemically and biologically oxidizible (Weiner, 2008). Moreover, significant quantity of organic matter can enter in to water bodies from urban and agricultural runoff (Harrison, 1990).

2.4.5 pH

Measurement of pH is one of the most important and frequently used tests in water chemistry. pH is an important factor in determining the chemical and biological properties of water. It affects the chemical forms and environmental impacts of many chemical substances in water. For example, many metals dissolve as ions at lower pH values, precipitate as hydroxides and oxides at higher pH, and re-dissolve again at very high pH. The pH value is an indicator of the chemical state in which these compounds will be found and must be considered when establishing water quality standards. The pH of pure water at 25^{o}C is 7.0, but the pH of environmental waters is affected by dissolved CO_2 and exposure to minerals (WHO, 2011; Pradhan and Pirasteh, 2011; Weiner, 2008).

2.4.6 Alkalinity

The alkalinity of water is a measure of its capacity to neutralize acids. Alkalinity is a measure of the water ability to absorbed H^+ without significant pH change. That is, alkalinity is a measure of buffering capacity of water. It is the sum of all the titrable bases. The major portion of alkalinity in natural water is caused by hydroxide, carbonate, and bicarbonate.For practical purposes, alkalinity due to other materials in natural water is insignificant and may be ignored (Maiti, 2004). The results of alkalinity in this study are reported as mg $CaCO_3$ per liter of water and calculated as total Alkalinity (mg/L as $CaCO_3$).

2.4.7 Hardness

Hardness is often referred to as the soap consuming property of water. Hardness may be divided into two types, carbonate and non-carbonate. Total hardness (as $CaCO_3$) = 2.497 (Ca^{2+}, mg/L) + 4.118 (Mg^{2+}, mg/L). Carbonate hardness includes portions of Ca and Mg, and certain amount of bicarbonates. Hardness caused by Ca and Mg is usually indicated by precipitation of soap scum and the need for excess use of soap to achieve cleaning. The taste threshold for the Ca ion is in the range of 100 – 300 mg/L, depending on the associated anion, and the taste threshold for Mg is probably lower than that for Ca. In some instances, consumers tolerate water hardness in excess of 500 mg/L (WHO, 2011; Pradhan and Pirasteh, 2011; Ethiopian Water Technology Centre, 2008). As with alkalinity, hardness is usually expressed as an equivalent concentration of $CaCO_3$. However, hardness is a property of cations (Ca^{2+} and Mg^{2+}) while alkalinity is a property of anions (HCO_3^- and CO_3^{2-}) (Weiner, 2008).

2.5 Major Chemical Parameters

Major chemical parameters are those most often present in natural waters in concentrations greater than 1.0 mg/L. These are the cations Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} and the anions Cl^{-}, NO_3^{-}, PO_4^{3-}, and SO_4^{2-}(Weiner, 2008; USEPA, 2006).

2.5.1 Calcium and Magnesium

Calcium (Ca): Ca is an essential nutrient for plants and animals, essential for bone, nervous system, and cell development. Recommended daily intakes for adults are between 800 and 1200 mg/day. Most of this is obtained in food; drinking water typically accounts for 50–300 mg/day, depending on the water hardness and assuming ingestion of 2 L/day. Ca in food and water is essentially nontoxic. A number of studies suggest that water hardness protects against cardiovascular disease. One possible adverse effect from ingestion of high concentrations of Ca for long periods of time may be a greater risk of kidney stones. The presence of Ca in water decreases the toxicity of many metals to aquatic life. Thus, the presence of Ca in water is beneficial and no limits on Ca have been established for protection of human or aquatic health (Weiner, 2008; USEPA, 2006).

Magnesium (Mg): Mg is an essential nutrient for plants and animals, essential for bone and cell development. Recommended daily intake for adults is 400–450 mg/day, of which drinking water can supply from 12 to 250 mg/day, depending on the Mg concentration and assuming ingestion of 2 L/day. In general, the presence of Mg in water is beneficial and no limits on Mg have been established for protection of human or aquatic health (Weiner, 2008). There are no primary or secondary drinking water standards for Mg. Mg in drinking water may provide nutritional benefits for persons with Mg deficient diets (USEPA, 2006).

2.5.2 Sodium and Potassium

Sodium (Na): Na is an important constituent for determining the quality of irrigation water. Most Na salts are readily soluble in water, but take no active part in chemical reactions.Na has wide variations in its concentration in ground water (Pradhan and Pirasteh, 2011; Shah *et al*., 2011). The taste threshold concentration of Na in water depends on the associated anion and the temperature of the solution. At room temperature, the average taste threshold for Na is about 200 mg/L. No health-based guideline value has been derived for Na in drinking wate r, as the contribution from drinking-water to daily intake is small (WHO, 2011).

Potassium (K): K is an essential element in humans and other living organisms (Csuros and Csuros, 2002). K occurs widely in the environment, including all natural waters. It can also occur in drinking water as a consequence of the use of $KMnO_4$ as an oxidant in water treatment. In some countries, KCl is being used in ion exchange for household water softening in place of, or mixed with, NaCl, so K ions would exchange with Ca and Mg ions. Possible replacement or partial replacement of Na salts with K salts for conditioning desalinated water has been suggested. The latter seems to be an unlikely development at this stage, in view of the cost difference. Currently, there is no evidence that K levels in municipally treated drinking water, even water treated with $KMnO_4$, are likely to pose any risk for the health of consumers. It is not considered necessary to establish a health based guideline value for K in drinking water. Consequently, no health-based guideline value established for K in drinking-water (WHO, 2011).

2.5.3 Chlorides

Chlorides are widely distributed in nature, usually in the form of Na, K, and Ca salts (NaCl, KCl and $CaCl_2$), although many minerals contain small amounts of chloride as an impurity. Chloride in natural waters arises from weathering of chloride minerals, salting of roads for snow and ice control, seawater intrusion in coastal regions, irrigation drainage, ancient groundwater brines, geothermal waters, and industrial wastewater. Concentrations in unpolluted surface waters and non-geothermal ground waters are generally low, usually below 100 mg/L. Thus, chloride concentrations in the absence of pollution are normally less than those of sulfate or bicarbonate. Chloride is the most abundant anion in the human body and is essential to normal electrolyte balance of body fluids. Chlorides in water are more of a taste than a health concern, although high concentrations may be harmful to people with heart or kidney problems. There are no primary drinking water standards for chloride. The EPA secondary standard for chloride is 250 mg/L, based on adverse effect on taste (WHO, 2011; Pradhan and Pirasteh, 2011; Weiner, 2008).

2.5.4 Nitrates

High nitrate concentrations in domestic water supplies can be toxic to human life. Nitrate is used mainly in inorganic fertilizers. In soil, fertilizers containing inorganic nitrogen and wastes containing organic nitrogen are first decomposed to give ammonia, which is then oxidized to nitrite and nitrate. The nitrate is taken up by plants during their growth and used in the synthesis of organic nitrogenous compounds. Surplus nitrate readily moves with the

groundwater. High concentrations of nitrate in surface or groundwater generally indicate agricultural contamination from fertilizers and manure seepage (California Department of Public Health, 2012; WHO, 2011). Drinking water standards for nitrate are strict because the nitrates can be reduced to nitrites, which oxidize iron in blood hemoglobin from ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). The resulting compound, called methemoglobin, cannot carry oxygen. The resulting oxygen deficiency is called methemoglobinemia. It is especially dangerous in infants (blue baby syndrome) because of their small total blood volume. A health-based guideline value for nitrate of 50 mg/L (expressed as nitrate ion) was recommended in the WHO Guidelines for drinking water quality to prevent methemoglobinemia(WHO,2011).

2.5.5 Phosphates

Phosphorus is an essential nutrient for aquatic plants and animals. Phosphate (PO_4^{3-}) at high concentration in water bodies accelerate the growth of microscopic (algae) to macroscopic (macrophytes) and excessive growth of these aquatic plants can causes eutrophication and this results in deficiency of dissolved oxygen (DO) which kills fishes and other aquatic fauna. Toxicity of PO_4^{3-} in humans includes impaired renal function, rhabdomyolysis and tumorolysis Syndrome. Sewage, detergent use and fertilizer runoff are common sources. Phosphorus is also a constituent of animal wastes (Chandra *et al*., 2012; Weiner, 2008). Compounds containing phosphorus that are of interest to water quality include Orthophosphates (all contain PO_4^{3-}), trisodium phosphate (Na_3PO_4), disodium phosphate (Na_2HPO_4), monosodium phosphate (NaH_2PO_4), and diammonium phosphate ($(NH_4)_2HPO_4$). Orthophosphates are soluble and are considered the only biologically available form. To measure total phosphate, all forms of phosphate are chemically converted to orthophosphates or hydrated forms (Weiner, 2008).

2.5.6 Sulphates

Sulfate (SO_4^{2-}) is found almost universally in natural waters at concentrations ranging from a few tenths to several thousand milligrams/liter. The highest concentrations are usually found in groundwater and are considered to be a mixture of SO_4^{2-} from atmospheric, geochemical, and biological sources. Approximately 30% of SO_4^{2-} in groundwater may be of atmospheric origin, and the remainder from geologic and biological processes. SO_4^{2-} ions are discharged

into surface water through industrial wastes and atmospheric deposition of SO_2 (USEPA, 2008). However, higher levels usually occur in groundwater from natural sources (WHO, 2004). The presence of SO_4^{2-} in drinking water can cause noticeable taste. It is generally considered that taste impairment is minimal at levels <250 mg/L (Pradhan and Pirasteh, 2011; WHO, 2011). And also, higher levels of sulfate in drinking water may result in gastrointestinal
effects (WHO, 2004).

2.6 Heavy Metals

Heavy metals are elements with high atomic weights that are generally toxic in relatively low concentrations to plant and animal life. They tend to accumulate in the food chain. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of essential metals, however, can be detrimental to the organism. Nonessential heavy metals of particular because of their toxicity are cadmium, chromium, mercury, lead, arsenic, and antimony (Weiner, 2008).

Heavy metals are intrinsic, natural constituents of our environment and generally present in small amounts in natural aquatic environments. The presence of these metals in aquatic systems originates from the natural interactions between the water, sediments and atmosphere with which the water is in contact. The concentrations fluctuate as a result of natural hydrodynamic chemical and biological forces (Odu *et al.*, 2011; Aderinola *et al.*, 2009). Heavy metals in waters can also be from natural or anthropogenic sources (Weiner, 2008).

2.6.1 Some Selected Trace Metals (Mn, Fe, Zn, Cu, Cr and Cd)

Manganese (Mn): Mn is one of the most abundant metals in Earth's crust, usually occurring with iron (WHO, 2011). It does not occur in nature as the elemental metal, but is found in various salts and minerals, frequently along with iron compounds. Soils, sediments, and metamorphic and sedimentary rocks are significant natural sources of Mn (Weiner, 2008). Manganese naturally occurs in many surface and groundwater sources, particularly in anaerobic or low oxidation conditions, and this is the most important source of Manganese in drinking-water (WHO, 2004). Mn seldom reaches concentrations of 1.0 mg/L in natural

surface waters, and is usually present in quantities of 0.2 mg/L or less. Concentrations higher than 0.2 mg/L may occur in ground waters and deep stratified lakes and reservoirs under reducing conditions. Subsurface and acid mine waters may contain 10 mg/L. Mn is similar to Fe in its chemical behavior, and is frequently found in association with Fe. In natural waters, a substantial fraction of Mn is present in suspended form. In surface waters, divalent manganese (Mn^{2+}) is rapidly oxidized to insoluble manganese dioxide (MnO_2), which then precipitates as a black solid often observed as black stains on rocks. In drinking water distribution systems, precipitation of MnO_2 may cause unsightly black staining of fixtures and laundry (WHO, 2011: Weiner, 2008).

Health Concerns of Mn: Mn is an essential element for humans and animals. No health-based guideline value for Mn in drinking-water is proposed since it is not of health concern at levels found in drinking-water (WHO, 2011). Mn is a ubiquitous element that is essential for normal physiologic functioning in all animal species. Health problems in humans may arise from both deficient and excess intakes of Mn. Thus any quantitative risk assessment for Mn must consider that, although Mn is an essential nutrient, excessive intake causes toxic symptoms (Weiner, 2008). Manganese is known to cause neurological effects following inhalation exposure, and there have been epidemiological studies that report adverse neurological effects following extended exposure to very high levels in drinking water (WHO, 2004; Fifield and Haines, 1995).

Iron (Fe): Fe is one of the most abundant heavy metal in Earth's crust. Its chief ores are the red-orange hematite(Fe_2O_3) and the black magnetite(Fe_3O_4). Fe contains both the +2 and +3 oxidation states (Csuros and Csuros, 2002). Fe is found in natural fresh waters at levels ranging from 0.5 to 50 mg/L. Fe may also be present in drinking waters a result of the use of Fe coagulants or the corrosion of steel and cast iron pipes during water distribution. Fe is an essential element in human nutrition, particularly in the Fe(II) oxidation state (WHO, 2011).

Health Concerns of Fe: Fe may affect acceptability of drinking water. However, it is not of health concern at levels causing acceptability problems in drinking water. Therefore, no health-based guideline value for Fe in drinking water is proposed. The taste and appearance of drinking-water will usually be affected at levels above 0.3 mg/L Fe (WHO, 2011).

Zinc (Zn): Zn is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. The diet is normally the principal source of Zn. Although levels of Zn in surface water and groundwater normally do not exceed 0.01 and 0.05 mg/L,

respectively, concentrations in tap water can be much higher as a result of dissolution of Zn from pipes. It was considered that the derivation of a formal guideline value for Zn is not required. However, drinking water containing Zn at levels above 3 mg/L may not be acceptable to consumers (WHO, 2011; Csuros and Csuros, 2002).

Health Concerns of Zn: Zn may affect acceptability of drinking water. However, no health-based guideline value has been proposed for zinc in drinking water since it is not of health concern at levels found in drinking-water (WHO, 2011).

Copper (Cu): Cu is both an essential nutrient and a drinking water contaminant. Cu in a drinking water supply usually arises from the corrosive action of water leaching Cu from Cu pipes in buildings. High concentrations can interfere with the intended domestic uses of the water. Staining of sanitary ware and laundry may occur at Cu concentrations above 1 mg/L. At levels above 5 mg/L, Cu also imparts a color and an undesirable bitter taste to water. Although Cu can give rise to taste, it should be acceptable at the health-based guideline value of 2 mg/L (WHO, 2011).

Health Concerns of Cu: Cu is an essential nutrient, but at high doses it has been shown to cause stomach and intestinal distress, liver and kidney damage, and anemia. Persons with Wilson's disease may be at a higher risk of health effects due to Cu than the general public.
There is inadequate evidence to state whether or not Cu has the potential to cause cancer from a lifetime exposure in drinking water (Weiner, 2008; USEPA, 2006).

Chromium (Cr): Cr is widely distributed in Earth's crust. It occurs in minerals mostly as chrome iron ore, or chromite ($FeCr_2O_2$), in which it is present as Cr (III). Cr in soils occurs mostly as insoluble chromium oxide (CrO_3), where it is present as Cr (VI). In natural waters, dissolved Cr exists as either Cr^{3+} cations or in anions such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), where it is hexavalent with oxidation number +6. Though widely distributed in soils and plants, it generally is present at low concentrations in natural waters. Background levels in water typically range between 0.2 and 20 µg/L, with an average of 1 µg/L (Weiner, 2008).

Health Concerns of Cr: Trivalent Cr is an essential trace nutrient, and plays a role in prevention of diabetes and atherosclerosis. The harmful effects of Cr to human health are caused by hexavalent Cr. Since oxidants such as chlorine or ozone readily oxidize trivalent Cr to the toxic hexavalent form, water quality limits are usually written for total Cr

concentrations (Weiner, 2008). USEPA (2006) has found Cr to potentially cause the health effect like skin irritation from acute exposures at levels above the MCL.Long term exposures to Cr at levels above the MCL have the potential to cause dermatitis and damage to liver, kidney, circulatory and nerve tissues. USEPA recommended a MCL of 0.1 mg/L as a total concentration of Cr for drinking water (USEPA, 2006). WHO (2011) recommended a MCL of 0.05 mg/L as a total concentration of Cr for drinking water.

Cadmium (Cd): Cadmium is a non-essential trace metal for plants and animals (APHA, 1998). It is widely used in metal plating, steel industry and its compounds are widely used in batteries (Manahan, 2000). Cd is usually present in all soils and rocks. It occurs naturally in Zn, Pb, and Cu ores, in coal and other fossil fuels and shales. It often is released during volcanic action. These deposits can serve as sources to ground and surface waters, especially when in contact with soft, acidic waters. The adsorption of Cd onto soils and silicon or aluminum oxides is strongly pH-dependent, increasing as conditions become more alkaline. When the pH is below 6.5, Cd is desorbed from these materials. The oxide and sulfide are relatively insoluble whereas the chloride and sulfate salts are soluble. Soluble Cd compounds have the potential to leach through soils to groundwater (Weiner, 2008; Csuros and Csuros, 2002).Average concentrations in U.S. waters is about 0.001 mg/L. Cd concentrations in bed sediments are generally at least 10 times higher than in overlying water. Because Cd is chemically similar to Zn, an essential nutrient for plants and animals, it is readily assimilated into the food chain. Plants absorb Cd from irrigation water. The recommended upper limit in irrigation water is 0.01 mg/L (Weiner, 2008).

Health Concerns of Cd: Acute exposure of Cd can cause nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock, and renal failure. Long-term exposure to low levels of Cd in air, food, and water leads to a build-up of Cd in the kidneys and possible kidney disease. Other potential long-term effects are fragile bones and damage to lungs, liver, and blood (Weiner, 2008). USEPA (2006) primary drinking water standard for Cd is 0.005 mg/L and WHO (2011) recommended guideline value for Cd in drinking water is 0.003 mg/L.

2.6.2 Atomic Absorption Spectrophotometric Analysis of Heavy Metals

2.6.2.1 Principles of AAS

In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomized.
A light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used; this makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range (APHA, 1999; Jeffery *et al*., 1989).

2.6.2.2 Digestion Methods for Heavy Metal Analysis

Sample (matrix) digestion plays a central role in almost all analytical processes. Wet digestion with oxidizing acids is the most common sample preparation procedure. Sample wet digestion is a method of converting the components of a matrix into simple chemical forms. This digestion is produced by supplying energy, such as heat; by using a chemical reagent, such as acids. Where reagent is used, its nature will depend on that of the matrix.The amount of reagent used is dictated by the sample size which, in turn, depends on the sensitivity of the method of determination. Wet digestion has the advantage of being effective on both inorganic and organic materials. It often destroys or removes the sample matrix, thus helping to reduce or eliminate some types of interference (Mester and Sturgeon, 2003; Barcelo, 2000).

Water Sample Digestion

Samples are acidified with HNO_3/HCl or with HNO_3 and HCl and heated on a hotplate to reduce the volume to a defined level. After filtration, the samples are ready for analysis by atomic absorption spectrophotometer (Maiti, 2004). The relatively clean water sample such as groundwater or the tap water sample does not require acid digestion (Zhang, 2007).

Quality of Spring Water

Good-quality drinking water may be consumed in any desired amount without adverse effect on health. Such water is called 'potable'. It is free from harmful levels of impurities such as bacteria, viruses, minerals, and organic substances. It is also aesthetically acceptable and is free of unpleasant impurities, such as objectionable taste, color, turbidity, and odor. As fresh water supplies are further stretched to meet the demands of industry, agriculture and an ever-expanding population, the shortage of safe and accessible drinking water will become a major challenge in many parts of the world and there is a growing concern for the safety and quality of drinking water. The most common problems in household water supplies may be attributed to hardness, iron, sulfides, sodium chloride, acidity, and disease-producing pathogens, such as bacteria and viruses (Mahmoud et al., 2001). The purity of drinking water also depends on the sources and water type. The water used may be from any source, including spring water, well purified water, municipal water, or even untreated or contaminated water (Calderon,2000). Because of the large number of possible hazards in drinking water, the development of standards for drinking water requires significant resources and expertise, which many countries are unable to afford. Fortunately, guidance is available at the international level. The World Health Organization (WHO) publishes guidelines for drinking-water quality which many countries use as the basis to establish their own national standards. The guidelines represent a scientific assessment of the risks to health from biological and chemical constituents of drinking water and of the effectiveness of associated control measures. When adapting the guideline values to national standards WHO recommends that social, economic and environmental factors are taken into account through a risk-benefit approach. Many countries regulate the quality of water through government standards, typically used to ensure that water quality is safe (UN World Water Development Report, 2006).

3. MATERIALS AND METHODS

3.1 Description of the Study Area

The study area is situated in Hericha kebele rural association in Haru district, West Wollega Zone. There are about eleven known water springs in this rural area. To investigate the quality of spring waters in this area four springs (Abba Fasige, Mumme, Abba Nura, and Chirecha) were considered for selected physico-chemical parameters, and certain heavy metals.

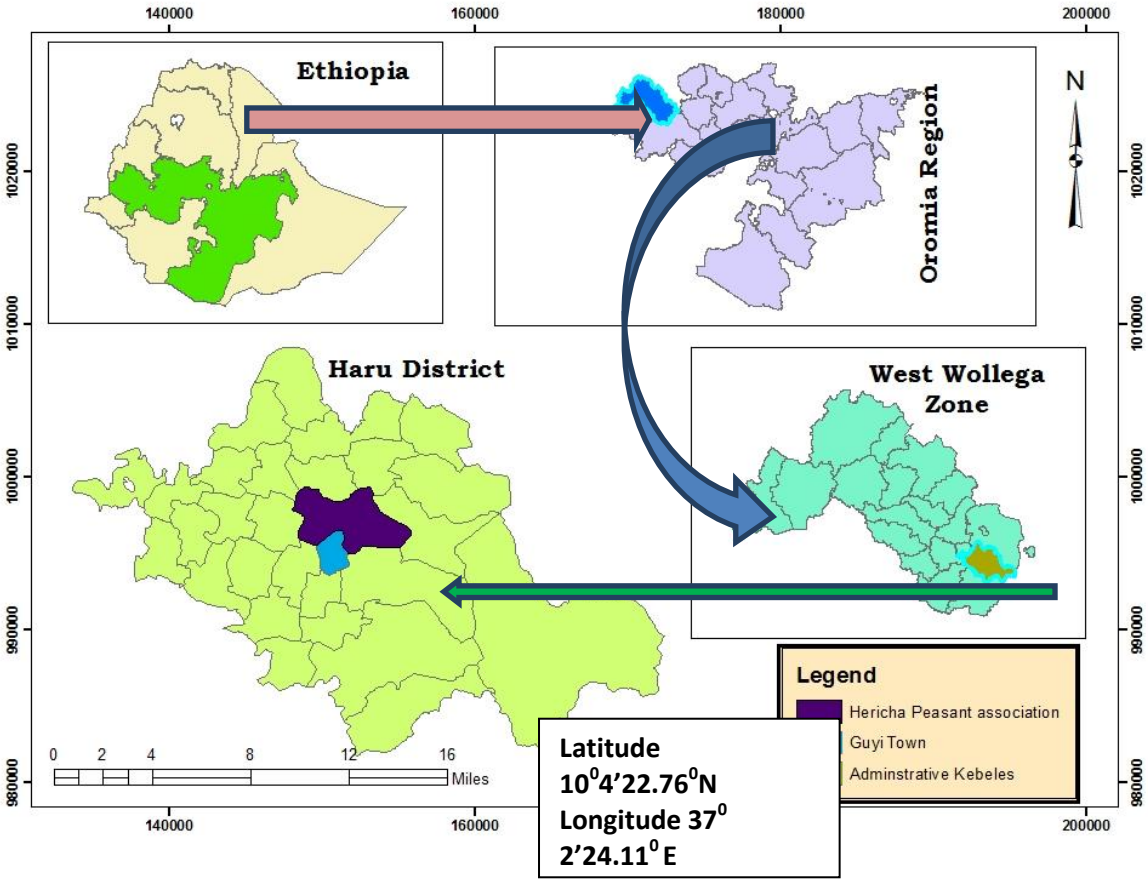

Figure 1: Map of the study area
Source: Central Statistics Agency of Ethiopia 2012

Table 1: Description of location (coordinate) of the study spring sites

Spring sites	Location (coordinate)	Elevation point	Distance interval	Activities around the springs
Abba Fasige(S_1)	Latitude: 08° 59.929'N Longitude : 035° 49.347'E	1906m	The distance between S_1 and S_2 is 0.9 km	Livestock Human Agriculture
Mumme(S_2)	Latitude : 08° 59.819'N Longitude : 035° 49.660'E	1895m	The distance between S_2 and S_3 is 1.2 km	Agriculture Livestock Human
Abba Nura(S_3)	Latitude : 09° 00.125'N Longitude : 035° 49.501'E	1920m	The distance between S_3 and S_4 is 1km	Human Livestock
Chirecha(S_4)	Latitude : 08° 59.806'N Longitude : 035°49.065'E	1904m	The distance between S_4 and S_2 is 1.5km	Agriculture Livestock Human

3.2 Glass wares, Instruments and Chemicals

3.2.1 Glass wares and Instruments

Polyethylene bottles, polyethylene bags, Ice-box, a mercury thermometer (0-100^{o}C), a pH-meter (ELMEIRON® Zabrze-Grzybowice, POLAND), a portable conductivity meter (ELMEIRON® Zabrze-Grzybowice, CC-101, POLAND), volumetric flasks (50, 100, 250, 500 and 1000 mL), volumetric pipettes (1, 5 and 10 mL), burette (50 mL), measuring cylinder (10, 25 and 50 mL), Erlenmeyer flasks (150 mL), beakers (250 mL), a hot plate (Corning® Hotware, PC-200/210/220, Germany), COD Reflux apparatus consisting of a flat bottom 500-mL capacity flask with condenser, a heating mantle, a 0.45-µm type membrane filter paper (Whatman®, No. 41, England), Electric Blast Drier (101-0, Tianjin Taisite Instrument± Co. Ltd, China), a mortar with pestle, electronic analytical balance with 0.00001g precision (AA200DS, Denver Instrument Company, United States), Conductivity /TDS/ Salinity/ Resistivity Meter (SCHOTT-GERATE GmbH. Hattenbergstr.10, SX713, TDS working range: 0-100 g/L, China), Electrical Thermostatic Water Bath (DK-2000-

IIIL,Tianjin Taisite Instrument Co. Ltd , China), ESCO FRONTIER LABORATORY FUME HOOD (Model: EFH-4A1), ELICO-CL 378 Flame Photometer, ELICO-SL 194 Double Beam Atomic Absorption Spectrophotometer, and ELICO-SL 160 Double Beam UV-Vis Spectrophotometer were used.

3.2.2 Chemicals

HNO_3 (65.0−68.0%, UNI-CHEM® Chemical reagents, India), $HClO_4$ (70.0-72.0%, UNI-CHEM® Chemical reagents, India) and 30.0% H_2O_2 (UNI-CHEM® Chemical reagents, India) were used for the sample digestions. Copper foil (99%, LOBA CHEMIE PVT.LTD.INDIA), metallic Zn (99.5%, LOBA CHEMIE PVT.LTD.INDIA), K_2CrO_4 (99.5%, UNI-CHEM® Chemical reagents, India), NaCl (99.80%, UNI-CHEM® Chemical reagents, India), KNO_3 (99%, General Purpose Reagent, BDH Chemicals Ltd, Poole, England) and anhydrous extra pure K_2HPO_4 (98-99%, KIRAN LIGHT LABORATORIES™) were used for the preparation of Cu, Zn, Cr, Na, K , NO_3^- and PO_4^{3-} stock standard solutions, respectively. Disodium salt of EDTA (99%, UNI-CHEM® Chemical reagents, India), EBT (99.5%, UNI-CHEM® Chemical reagents, India), Na_2CO_3 anhydrous (99%, Scientific Limited Northampton, United Kingdom) and $CaCO_3$ (96%, FINKEM, Analytical grade crystals) were used for determination of total hardness.

H_2SO_4 (96.0-98.0%UNI-CHEM® Chemical reagents, India) were used for determination of total alkalinity. $AgNO_3$ (99%, LOBA CHEMIE PVT.LTD. INDIA) was used for argentometric titration for the determination of chloride. $K_2Cr_2O_7$ (99.8%, UNI-CHEM® Chemical reagents, India), Fe $(NH_4)_2(SO_4)_2.6H_2O$ (UNI-CHEM® Chemical reagents, India), $HgSO_4$ (95%, FINKEM, Analytical grade crystals) and $AgSO_4$ (UNI-CHEM® Chemical reagents, India) were used for COD determination. $BaCl_2$ (UNI-CHEM® Chemical reagents, India) was used for determination of SO_4^{2-}. Distilled water was used for all preparations and dilutions of solutions.

3.3 Sampling Procedures

3.3.1 Cleaning of sampling equipment

All polyethylene bottles used for water sampling were thoroughly washed with tap water and detergent, rinsed with distilled water and then soaked with 10% (v/v) HNO_3 for 24 hrs. In this case10% (v/v) HNO_3 were served to remove any traces of surface dirt and /or oil. After that, all containers were well-rinsed with distilled water routinely, air dried, and stored with the

caps on to prevent contamination. The containers were rinsed with sample water prior to actual sample collection before being used for sampling (APHA, 1999).

3.3.2 Water sampling, preservation and transportation

Representative water samples from sampling sites were collected into 2L polyethylene bottles by composite sampling technique, using the same sampling protocol at all sites, i.e., the samples were taken in the morning, in the afternoon and late afternoon from each spring sites and then composite in to 2L polyethylene bottles. The water samples then were preserved at a temperature of $4^{o}C$ prior to analysis to avoid microbial action affecting their concentration(APHA, 1999) . The collected samples were stored in an ice-box and transported to chemistry department laboratory of Addis Ababa University and water quality section of Ethiopia Construction Design and Supervision Works Corporation for analysis.

3.4 Sample Analysis

3.4.1 Temperature

Temperature was measured with a mercury thermometer ($0\text{-}100^{o}C$). Readings were made with the thermometer immersed in water long enough to permit complete equilibration (APHA, 1999).

3.4.2 pH

pH was measured with a portable pH-meter. The pH-meter was calibrated with a buffer solution of pH 7.0 according to the procedures given on the manufacturer's instruction manual. One buffer tablet was dissolved in a 100 mL volume of distilled water to prepare the buffer solution. The pH-meter was calibrated before and after measurements prior each site of water samples.

3.4.3 Electrical conductivity

EC was measured with a portable conductivity meter following the procedures given in the manufacturer's instruction manual.

3.5 Laboratory Sample Analysis

3.5.1 Calibration of analytical balance

AA-200DS Model electronic analytical balance was calibrated first properly using a known 100 g calibration weight provided with the instrument by the manufacture.

3.5.2 Cleaning of laboratory glassware

All the glass wares and apparatus used through the entire analysis were first washed with tap water and detergent. Next, rinsed with distilled water and followed by 10% (v/v) HNO_3 solution. Finally, rinsed again with distilled water and air dried to ensure that free from contamination.

3.5.3 Calibration of Conductivity/TDS/Salinity/Resistivity Meter

TDS in water samples was measured with Conductivity/TDS/Salinity /Resistivity Meter as soon as the samples were transported to the laboratory. The device was calibrated with 0.01 M KCl solution following the procedures given in the manufacturer's instruction manual before the measurements were made.

3.5.4 Classical and Instrumental Methods of Analysis

3.5.4.1 Classical methods

All parameters including COD (Open Reflux Method 'Section 5220 B.4*b'*), total hardness (EDTA Titrimetric Method 'Section 2340 C'), calcium (EDTA Titrimetric Method 'Section 3500-Ca B'), magnesium (Calculation Method 'Section 3500-Mg B'), and chloride (Argentometric Method 'Section 4500-Cl^- B') were analyzed following the procedures given by a standard method (APHA, 1999). Total alkalinity was determined by titrimetric method following the procedure given by handbook of methods in environmental studies (Maiti, 2004).

Chemical oxygen demand (COD): The COD of a water sample can be estimated using a standard method—a potassium dichromate digestion in an open-reflux condenser followed by titration with ferrous ammonium sulfate (FAS) and calculated as follows:

$$\text{COD as mg } O_2/L = \frac{(A-B) \times N \times 8{,}000}{\text{Volume(mL) of water sample}} \quad \textbf{.....(3.1)}$$

where A is the ml of FAS used for blank, B is the ml of FAS used for your water sample, and

N is the normality of FAS (Zhang, 2007).

Total Alkalinity (TA): The results of alkalinity are usually reported as mg $CaCO_3$ per liter of water and calculated as follows:

$$Phenolphthalein\ alkalinity,\ (mg\ CaCO_3)/_L = \frac{C \times N \times 50{,}000}{V} \quad \text{.....(3.2)}$$

$$\text{Total alkalnity, } (\text{mg } CaCO_3)/_L = \frac{(C + D) \times N \times 50{,}000}{V} \quad \text{.....(3.3)}$$

where C is the volume in ml of HCl solution used to reach pH = 8.3, D is the volume in ml of HCl solution used to reach pH = 4.4, N is the concentration of standard HCl solution in normality, and V is the volume of sample in ml (Zhang, 2007; Weiner, 2008).

Total Hardness (TH)

TH was determined by EDTA titration method and calculated by using the following equation:

$$\textbf{Total hardness as mg } CaCO_3/_{\textbf{L}} = \frac{\text{A} \times \text{B} \times 1000}{\text{mL of Sample}} \quad \text{.....(3.4)}$$

Where, A is the volume in mL of 0.01M EDTA required by sample for titration and B is the mg $CaCO_3$ equivalent to 1mL EDTA titrant (APHA, 1999).

Calcium (Ca) and Magnesium (Mg)

Ca is determined by EDTA titration method and calculated in mg/L by using the following formula:

$$\textbf{mg Ca}/_{\textbf{L}} = \frac{\text{A} \times \text{B} \times 400.8}{\text{mL of Sample}} \quad \text{.....(3.5)}$$

Where, A is the volume in mL of 0.01M EDTA required by sample for titration and B is the mg $CaCO_3$ equivalent to 1mL EDTA titrant (APHA, 1999).

Mg is calculated from the Ca concentration and TH, using the following equation:

$$\textbf{Mg(in mg/L)} = (\textbf{TH (mg } CaCO_3\textbf{/L)} - 2.497(\textbf{ Ca}, \tfrac{\text{mg}}{\text{L}}))/4.118 \quad \text{..... (3.6)}$$

Chloride (Cl^-): The Cl^- ion was determined by argentometric method and calculated according to the following formula:

$$\textbf{Cl}^- \textbf{ (in mg/L)} = \frac{(\text{A}-\text{B}) \times \text{N} \times 35{,}450}{\text{Volume(mL) of Sample}} \quad \text{..... (3.7)}$$

where A is the volume in mL of 0.0141N $AgNO_3$ for sample, B is the volume in mL of

0.0141N $AgNO_3$ for blank, and N is the normality of $AgNO_3$ (APHA, 1999).

3.5.4.2 Instrumental methods

The SO_4^{2-} ion was analyzed by direct reading spectrophotometer. For the determination of heavy metals two methods were selected: iron by spectrophotometer and Mn, Cu, Zn, Cr, and Cd by Flame Atomic Absorption Spectroscopy (FAAS), flame photometer (for Na and K analysis), and UV-Vis spectrophotometers (for PO_4^{3-} and NO_3^- analysis) were used.

3.5.4.2.1 Spectrophotometer

The Hach DR2000 Direct Reading Spectrophotometer was used to analyse iron and sulphate ion concentration in the water sample.

3.5.4.2.2 Analysis of SO_4^{2-} (by turbidimetric method followed by spectrophotometer)

The turbidimetric method of measuring sulphates based up on the fact that barium sulphate was tended to precipitate in a colloidal form of uniform size and this tendency was enhanced in presence of a magnesium chloride, hydrochloric acid, and glycerol which is called conditioning reagent..

$$SO_4^{2-} + BaCl_2 \rightarrow BaSO_4\downarrow$$

The absorbance of the barium sulphates formed was measured by a spectrophotometer at 420 nm and the sulphate ions concentration was determined by comparison of the reading with the standard curve. The SO_4^{2-} is determined by turbidimetric method and calculated using the following formula:

$$\mathbf{SO_4^{2-}\ (in\ mg/L)} = mg\ SO_4^{2-} \times 1000/mL\ of\ sample \quad \text{.....(3.8)}$$

Standard sulphate solution

1.479g an hydrous sodium sulphate was weighed accurately and dissolved in distilled water. A 1000 mL standard measuring flask was taken and placed a funnel over it. Then the solution was transferred to the flask and made up to 1000 mL using distilled water (1mL = 1mg SO_4^{2-}).

3.5.4.2.3 Analysis of iron(by spectrophotometer)

Reagent and chemicals

Ferrover iron reagent and 1,10-phenonthroline indicator were used to analyze total iron. Ferrover reagent converted all soluble iron and most insoluble form of iron in the sample to soluble ferrous iron. The ferrous iron was reacted with 1,10-phenanthroline indicator in the reagent to form an orange color in proportion to the iron concentration.

3.5.4.2.4 Instruments Working Conditions

Table 2: Instruments operating conditions for calibration and sample analysis.

FAAS Working Conditions

Element	Wavelength (nm)	Slit Width (nm)	Lamp Current (mA)	Oxidant/Fuel
Cu	324.7	2.000	10.0	Air/Acetylene
Mn	403.1	2.500	11.0	Air/Acetylene
Cr	357.9	2.000	10.6	Air/Acetylene
Cd	326.1	2.500	8.0	Air/Acetylene
Zn	213.9	0.700	10.0	Air/Acetylene

Spctrophotome tric Working Condition

Parameter	Wavelength (nm)	Band Pass (nm)	Cell Type	Cell Length (cm)
NO_3^-	220 and 275	1.8	Quartz	1.0
PO_4^{3-}	690	2.6	Quartz	1.0

Flame Photometric Working Conditions

	Wavelength (nm)	Flame System
Na	589	Air/C_4H_{10}
K	769	Air/C_4H_{10}

3.5.4.2.5 Preparation of stock solutions

Metal stock standards

For Mn, and Cd commercially available 1000 mg/L solutions were used. For Cu and Zn 1000 mg/L solutions were prepared by dissolving 1.0 g Cu metal and 1.0 g Zn metal in 20 ml conc.HNO_3, and 17 mL HCl, and diluting to 1000 mL with distilled water , respectively. For Cr 1000 mg/L solution was prepared by dissolving 3.7348 g K_2CrO_4 in distilled water and diluting to 1 L. For Na, 1000 mg/L solution was prepared by dissolving 2.5418 g NaCl dried at 140 ^oC, in distilled water, and diluting to 1 L. For K, 1000 mg/L solution was prepared by dissolving 1.907 g KCl dried at 110 ^oC, in distilled water and diluting to 1 L.

Reagents Preparation for Phosphate and Nitrate Analysis

All reagents were prepared according to the procedures given in Standard Methods; '4500-PD. Stannous Chloride Method for phosphate', and '4500-NO_3^- B. Ultraviolet Spectrophotometric Screening Method for nitrate' (APHA, 1999).

3.5.4.2.6 Intermediate standard solutions

The intermediate metal standard solutions (100 mg/L, each) were prepared by taking 10 mL of Individual metal stock solutions in a separate 100 mL volumetric flasks and diluting to the mark with distilled water.

3.5.4.2.7 Calibration standard solutions

The calibration standard solutions were used to calibrate the instrument response with respect to the analyte concentration. The calibration standard solutions that were used for the calibration curves are the already prepared calibration standard solutions in the laboratory of sample analyzed. Standard solutions of four points (including calibration blank) were prepared for Mn, Cu, Na, and K. Standard solutions of five points (including calibration blank) were prepared for Zn, Cd and Cr. Standard solutions of six points (including calibration blank) were prepared for NO_3^- , PO_4^{3-} and SO_4^{2-}.The calibration standard concentrations within the working linear range of the instrument used for analysis. The prepared calibration standards: calibration blank (S_0), standard 1 (S_1), standard 2 (S_2), standard 3 (S_3) for Mn, Cu, Na and K; calibration blank (S_0), standard 1 (S_1), standard 2(S_2),standard 3(S_3) and standard 4 (S_4) for Zn, Cd and Cr ; and calibration blank(S_0),standard 1(S_1), standard 2(S_2),standard 3(S_3), standard 4(S_4) and standard 5(S_5) for NO_3^-, PO_4^{3-} and SO_4^{2-} are given in Table 3.

Table 3: calibration standards for Mn, Cd, Cu, Cr, Zn, Na, K, NO_3^- and PO_4^{3-}.

Analyte	Calibration Standard Solutions (mg/L)					
	S_0	S_1	S_2	S_3		
Mn	0.0	2.0	5.0	10.0		
Cu	0.0	0.5	1.0	2.0		
Na	0.0	5.0	10.0	20.0		
K	0.0	5.0	10.0	20.0		
	S_0	S_1	S_2	S_3	S_4	
Zn	0.0	0.25	0.5	0.75	1.0	
Cd	0.0	0.25	0.5	1.0	2.0	
Cr	0.0	1.0.	2.0	3.0	4.0	
	S_0	S_1	S_2	S_3	S_4	S_5
SO_4^{2-}	0.0	5.0	10.0	15.0	20.0	25.0
NO_3^-	0.0	0.5	1.0	1.5	2.0	2.5
PO_4^{3-}	0.0	0.25	0.5	0.75	1.0	1.25

3.5.4.2.8 Spiking metal standard mixture solution

Standard mixture solution consists of all the metals of interest at different concentrations (Cd = 25, Cu =100, Cr = 125, and Zn = 100 mg/L) were prepared by taking 2.5, 10, 12.5, and 10 mL of Cd, Cu, Cr, and Zn stock standard solutions (1000 mg/L), respectively, in to 100 mL volumetric flask and diluting to volume with distilled water(manufacturer's instructional manual).

3.5.4.2.9 Calibration blanks/instrument blanks

2% (v/v) HNO_3 was prepared as a calibration blank for Cu, Zn, Cd and Cr determination, respectively. Distilled water used as a calibration blank for Mn, Na, K, Fe, NO_3^-, and SO_4^{2-} determination. The differences in calibration blanks occurred due to all the parameters were not analyzed in only one laboratory. Distilled water treated with 4mL of ammonium molybdate solution and 0.5 of Stannous Chloride reagent were prepared as a calibration blank for PO_4^{3-} determination.

3.5.4.2.10 Water samples digestion procedure

Three replicates of 100 mL water samples (filtered through Whatman No. 41 filter paper) was taken into 150 mL Erlenmeyer flasks for each springs and acidified with 10 mL of conc. HNO_3. Then, the mixtures were heated to about 20 mL. Finally, the remaining part of the samples were cooled and diluted to 100 mL with distilled water in 100 mL volumetric flasks. The digestate was ready for FAAS analysis (USEPA Method 2002).

3.5.4.2.11 Estimation of detection limits

Instruments Detection Limit (IDL)

The IDL for each analyte was determined from six replicate measurements of their respective calibration blanks at their specific wavelengths (USEPA, 2007). The IDL was calculated by using the following equation.

IDL = SD X 3 **……..……..(3.9)**

Where, SD is the standard deviation of the six replicates of calibration blanks.

Methods Detection Limit (MDL)

For water samples analysis, the MDL of each analyte was determined from six replicate measurements of reagent water spiked with the target analyte at a concentration four times the IDL. A blank was also processed along with it to measure background contamination. The MDL was calculated by using the following equation:

MDL = SD X t **……...……..(3.10)**

Where SD is standard deviation, t is obtained from ‘‘Student’s t value Table’’, corresponding to n - 1 degree of freedom at a defined confidence level (APHA, 1999).

3.5.6 Evaluation of Analytical Precision, Accuracy and Recovery

The analytical method precision was assessed in terms of relative standard deviation (RSD) and standard deviations (SD) among measurements. The % recoveries were estimated according to the following equation (APHA, 1999):

$$\%\ \text{Recovery on spike} = \frac{Spiked\ sample\ value - sample\ value}{Spiked\ value} \times 100 \quad \textbf{……...….(3.11)}$$

The standard deviation was assessed using equation (APHA, 1999):

$$SD = \sqrt{\frac{\sum\left(xi - \bar{x}\right)^2}{n-1}} \quad \text{……..…. (3.12)}$$

3.5.7 One-way Analysis of Variance (ANOVA)

The obtained data was also treated with one-way ANOVA to assess the variations of the parameters among the spring water samples analyzed by using IBM SPSS Statistics 20 version software.

4. RESULTS AND DISCUSSION

4.1 Physico-chemical Parameters of Water Samples

The mean values were obtained from triplicate measurements. The results (mean ± SD) are given in Table 4.

Temperature: In this study the measurements were made during morning time, daytime and late afternoon, in the gap of 4 hours, to observe the diurnal variation in water temperature. Thus, the variation of the temperature during the investigation was small with the ranges of 1.4^{o}C, 1.7^{o}C, 3^{o}C, and 1.9^{o}C at site of Abba Fasige, Mumme, Abba Nura, and Chirecha , respectively. According to Weiner (2008), the maximum induced change in water temperature is limited to a 3^{o}C increase over a 4 hours period. Then, the observed variation for temperature on each site is below this limit and no changes harmful regarding the temperature of the studied water springs. The reported results (Table 4) are the average of the three time-gap measurements that were taken as the average of three replicates at each spring sources. Then, the measured temperature values were varied from 22.4^{o}C to 23.8^{o}C at Abba Nura; 23.2^{o}C to 24.9^{o}C at Mumme; 2.2^{o}C to 25.2^{o}C at Abba Nura; and 23.3^{o}C to 25.2^{o}C at Chirecha Spring. One-way ANOVA test ($p = 0.05$) showed that the temperatures varied significantly between the springs. This could be from the variation in air temperature and the amount of shade around the springs.

pH: The pH were also measured during morning time, daytime and late afternoon along with temperature and the average of the three time-gap measurements were reported (Table 4). The pH at-site of Abba Fasige, Mumme, Abba Nura, and Chirecha was ranged from 5.94 to 5.98, 5.97 to 5.99, 6.02 to 6.04, and 7.27 to 7.29, respectively. The obtained results indicated that all the four spring sources except one were below the limit or below in the range of WHO and different national standards for drinking water quality (Appendix I). This indicates that the corrosive ability of water on the piping system is to some extent large. On the other hand, the pH of Chirecha spring site is found within the limit of WHO and different national standards for drinking water quality (Appendix I). The results of one-way ANOVA ($p = 0.05$) indicated that the pH are significantly differ between the studied waters springs. This could be due to the variation of the natural dissolved inorganic carbon as CO_2 and combines with water to form carbonic acid.

Table 4: Mean* ± SD values for physico-chemical parameters of spring waters.

Parameter	Spring Sites			
	Abba Fasige	Mumme	Abba Nura	Chirecha
Temperature(℃)	23.3 ± 0.80	23.97 ± 0.86	23.67 ± 1.50	24.23 ± 0.95
pH	5.96 ± 0.02	5.98 ± 0.01	6.03 ± 0.01	7.28 ± .01
EC(μS/ cm)	81 ± 1.00	89.33 ± 1.53	56.67± 1.15	107.7 ± 0.57
TDS(mg/L)	54.67 ± 1.16	60.67± 1.16	38.67 ± 1.16	71.3 ± 1.55
COD(mg/L)	10.67 ± 1.15	8.67 ± 1.15	8.67 ± 1.15	10.67 ± 1.15
TA(as mg $CaCO_3$/L)	27.33± 1.15	22.67± 1.15	24.67± 1.15	38.67± 1.15
TH(as mg $CaCO_3$/L)	34.67± 1.20	40.907± 1.20	24.96± .00	49.92± 2.08

Mean values are calculated from three replicates.

Electrical Conductivity (EC): Like temperature and pH, the EC were also measured during morning time, daytime and late afternoon and the average of the three time-gap measurements were taken (Table 4). The mean values were found between the minimum mean 56.67 µS/cm (Abba Nura) and the maximum mean 107.67 µS/cm (Chirecha). The current study gave the results below the guidelines for drinking water quality (Appendix I). Therefore, no issues concerned with EC if the waters to be used for drinking.

Total Dissolved Solids (TDS): According to WHO (2011), the palatability of water with a TDS level of less than about 600 mg/L is generally considered to be good. The measured TDS values were distributed between the minimum mean value of 38.67 mg/L (Abba Nura) and the maximum mean value of 71.33 mg/L (Chirecha). The great differences in concentrations of TDS of Abba Nura and Chirecha spring water observed might be due to the differences in concentrations of potassium, magnesium, calcium, nitrate, phosphate and chloride ions in the two spring sites i.e. the concentrations of K^+ , Mg^{2+}, Ca^{2+}, NO_3^-, PO_4^{3-}, and Cl^- ions in Abba Nura are smaller than that of Chirecha spring water. The TDS values from each spring waters are below the WHO and different national guidelines for drinking water quality (Appendix I). This indicates that no palatability problem concerned with TDS of the studied waters.

Chemical oxygen demand (COD):

The COD mean values were included between the minimum value 8.67 mg/L (Abba Nura and Mumme) and maximum value 10.67 mg/L (Abba Fasige and Chirecha), as given in

Table 4. No COD standard has been prescribed by WHO (2011) and different national organizations (Appendix I). One-way ANOVA test (p = 0.05) showed that the COD values across the sampling sites were not statistically different. This is due to no variation of the organic and oxidizable inorganic matters between the water springs.

Total Alkalinity (TA): The obtained TA values are due to methyl orange alkalinity (at about pH 4.5) because the phenolphthalein alkalinity which is expected at about pH 8.3 in each sites are zero. As mentioned in literature part, the major portion of alkalinity in natural waters is caused by hydroxide, carbonate, and bicarbonate. According to the standard method (APHA, 1999), when P = 0 the OH^- alkalinity and CO_3^{2-} alkalinity are zero while HCO_3^- alkalinity is equal with TA.

Therefore, the observed alkalinity is possibly due to HCO_3^- from dissolved CO_2. The present study result of TA was found between the minimum mean of 22.67 mg/L (Mumme) and the maximum mean of 38.67 mg/L (Chirecha) as shown in Table 4. The results indicate that Chirecha spring contains high bicarbonates, which react with H^+ ions from the water thereby raising the pH of the water. The determined TA mean values for each spring site are below the maximum permissible value for drinking water (Appendix I). This indicates that no unpleasant taste associated with the alkalinity of the studied waters. The one-way ANOVA test (p = 0.05) revealed that the TA values across the sampling sites were statistically not different. This could be due to no variation of bicarbonate sources across the water springs.

Total Hardness (TH): The TH mean value was varied between the minimum mean value 24.96 mg/L in Abba Nura and the maximum mean value 49.92 mg/L in Chirecha (Table 4), and all are below the recommended drinking water quality standards (Appendix I). This indicates that no hardness related problems like scale formation in water pipes and soap consuming property of waters. The great differences in concentrations of TH of Abba Nura and Chirecha spring water observed might be due to the differences in concentrations of calcium and magnesium ions in the two spring sites i.e. the concentrations of Ca^{2+} and Mg^{2+} ions in Abba Nura are smaller than that of Chirecha spring water. The obtained results from one-way ANOVA test (p = 0.05) showed that the TH values across the sampling sites were statistically not different. This could be due to the concentration of the hardness causing cations and anions like Ca^{2+}, Mg^{2-}, Cl^- and HCO_3^-, were not vary among the analyzed water samples. In addition to that no any other condition (like factories) present in study area that discharge these ions to make hardness variation across the water springs.

4.2 Major Chemical Parameters of Water Samples by Classical Methods

Calcium (Ca) and Magnesium (Mg): The results are given in Table 5.The source of Ca and Mg is the rocks from which it is leached.

The Ca and Mg of the investigated spring waters could be due to the contact between the water body and the rock layers. Because these springs are naturally occurred springs that come out on the earth's surface by crossing rock layers which leach these minerals and others to the water body. The Ca mean values in each spring sites were ranged from the minimum value 4.71 mg/L (Abba Nura) to the maximum of 10.26 mg/L (Chirecha) and Mg mean values were ranged from the minimum value 3.16 mg/L (Abba Nura) to 5.82 mg/L (Chirecha) (Table 5). The study results for Ca and Mg are below the current recommended maximum value for drinking water (Appendix I). One-way ANOVA test ($p = 0.05$) for Ca and Mg showed that the Ca and Mg values across the spring sites were not statistically different. This is because no variation in total hardness among the water springs.

Sulphate (SO_4^{2-}): SO_4^{2-} is one of the major anions occurring in natural waters (Maiti, 2004). SO_4^{2-} in water is usually expected to atmospheric deposition, industrial runoff, and natural sources such as gypsum ($CaSO_4$. $2H_2O$) and anhydrite ($CaSO_4$) (Saadeh, 2012).The SO_4^{2-} in the studied spring waters might be due to atmospheric deposition of particulate matter of $SO_4^{2-}$from the investigated area and natural sources in the waters. The SO_4^{2-} ions in all springs were ranged from the mean values of 3.24 mg/L in Abba Fasige to 5.59 mg/L in Abba Nura(Table 5). The presence of SO_4^{2-} in drinking-water can cause noticeable taste. It is generally considered that taste impairment is minimal at levels below 250 mg/L. No health-based guideline value has been derived for sulfate (WHO, 2011). The investigated waters have SO_4^{2-} less than the taste threshold value (<250 mg/L) recommended by WHO (2011). Also on comparison with other guideline values for drinking water, no problem associated with SO_4^{2-} of the studied waters. One-way ANOVA test ($p = 0.05$) showed that the SO_4^{2-} concentrations among the studied water springs are significantly different.

Chloride (Cl^-): Chloride in drinking-water originates from natural sources, sewage and industrial effluents (WHO, 2011). Therefore, the Cl^- ions in the studied springs are possibly due to the natural sources since there are no available industrial sources from the study area. No health-based guideline value is proposed for chloride in drinking water. Because, no health concern at levels found in drinking-water (WHO, 2011).

The Cl^- concentration in the investigated water springs were ranged from the minimum mean value 3.92 mg/L in Abba Nura to 6.77 mg/L in Chirecha. Chloride may affect acceptability of drinking water by offering a salty taste to water. As reported in Table 5, the Cl^- values determined for all spring sources are below the current guideline values for drinking, indicating that no taste effects associated with the studied springs. One-way ANOVA test ($p = 0.05$) showed that the Cl^- values across the sampling sites were not statistically different. This indicates that there are no conditions created for the solubility of Cl^- salts and discharging chloride ions or salts of chloride ions in to the water samples in different ways.

Table 5: **Mean* ± SD (in mg/L) of major chemicals and heavy metals in water samples.**

Parameter	Spring Sites			
	Abba Fasige	Mumme	Abba Nura	Chirecha
Ca	7.21 ± 0.07	8.04 ±0.47	4.71± 0.47	10.3 ± 0.48
Mg	3.99 ± 0.50	4.99 ± 0.00	3.16 ± 0.28	5.82 ± 0.28
Cl^-	5.69 ± 0.617	4.63 ± 0.62	3.92 ± 0.61	6.77 ± 0.62
SO_4^{2-}	3.24 ± 0.26	3.54 ± 0.42	5.59 ± 0.23	4.42 ± 0.34
Na	3.12 ± 0.02	2.90 ± 0.00	4.94 ± 0.00	3.96 ± 0.10
K	1.40 ± 0.02	1.70 ± 0.01	0.79 ± 0.01	2.33 ± 0.07
NO_3^-	17.67 ± 0.07	32.2 ± 0.70	1.26 ± 0.02	27.6 ± 0.104
PO_4^{3-}	0.07 ±.00	0.07 ± 0.00	0.09± 0.00	0.34± 0.006
Cu	0.04 ± 0.001	0.05 ± 0.01	0.07± 0.01	0.06 ± 0.01
Mn	0.02 ± 0 .00	0.13 ± 0.01	0.03± 0.00	0.02 ± 0.01
Cd	< MDL	< MDL	< MDL	< MDL
Cr	< MDL	< MDL	< MDL	< MDL
Fe	0.03± 0.03	0.15 ± 0.03	0.08± 0.01	0.08 ± 0.03
Zn	0.70± .009	< MDL	0.65± 0 .07	0.55± 0.01

* Measurements were made in three replicates *

*<MDL: Less than Method Detection Limit.

4.3 Flame Photometric Analysis of Water Samples

Flame photometric method was used for the analysis of Na and K based on the principles of Emission of electromagnetic radiation in the visible and ultraviolet regions of the spectrum by atoms after electronic excitation in flames (Fifield and Kealey, 2000; Jeffery *et al*., 1989).

4.3.1 Sample Analysis

All the samples representing its respective spring site were analyzed by the validated analytical methods for the required analytes. The obtained results are given in Table 4. **Sodium (Na)**: The mean values are ranged from the minimum value of 2.90 mg/L in Mumme to the maximum value of 4.94 mg/L in Abba Nura (Table 5). These values are below the drinking water quality guideline value currently recommended by WHO and different national organizations (Appendix I), indicating no taste problems concerned with Na in the waters. One-way ANOVA test (p = 0.05) found that the Na concentrations between

the studied water springs varied significantly. This could be from the variation of cation exchange capacity of water, mainly with Ca and Mg, since there is a direct contact between the soils and the water bodies.

Potassium (K): From the current study, calculated average values of K concentrations for each spring was within the range of the mean value 0.79 mg/L in Abba Nura to the maximum mean value 2.336 mg/L in Chirecha (Table 5). All values are below the maximum value recommended for drinking water quality (Appendix I) indicating no health risks concerned with K at levels found in these waters. One-way ANOVA test (p = 0.05) found that concentrations of K between the water springs varied considerably. This might be due to the variation of naturally occurring K salts in these springs.

4.4 UV-Vis Spectrophotometric Analysis of Water Samples

UV-Vis Spectrophotometric method was used for the analysis of NO_3^- and PO_4^{3-} based on the principles of absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum resulting changes in the electronic structure of ions and molecules (Fifield and Kealey, 2000; Jeffery *et al*., 1989).

4.4.1 Method Validation

4.4.1.1 Calibration Curves

The Calibration curves which show absorbance versus concentration were constructed for all NO_3^- , PO_4^{3-} , and SO_4^{2-} through direct analysis of the instrument blank and five point calibration standards at a specified wavelength of the analytes. The calibration curves for these analytes show good correlation coefficients of 0.999 , 0.999 and 0.998 for NO_3^- , PO_4^{3-} and, SO_4^{2-} respectively,(Table 5) which are greater than the minimum acceptance value of 0.995 (APHA, 1999). This showed that there was a good linearity between prepared concentration and the absorbance which indicating the best working condition of the instrument. The calibration curves for all are given in Appendix II.

Table 6: **Calibration standards, calibration equation, correlation coefficient (r^2) for NO_3^- , PO_4^{3-} and SO_4^{2-}**

Analyte	Wave length(nm)	Prepared Conc.(in mg/L)	Absorbance	Correlation Coefficient of calibration curve(r^2)	Calibration equation
NO_3^-	220 and 275	0.5, 1, 1.5, 2, 2.5	0.015, 0.036, 0.061, 0.082, 0.105	0.999	y = 0.045x - 0.008
PO_4^{3-}	690	0.25, 0,5, 0.75, 1, 1.25	0.079, 0.215, 0.351,0.477, 0.603	0.999	y = 0.524x - 0.048
SO_4^{2-}	420	5, 10,15,20,25	0.078, 0.152, 0.255, 0.299, 0.387	0.998	y= 0.015x- 0.0013

4.4.2 Sample Analysis

Nitrate (NO_3^-). NO_3^- can reach both surface water and groundwater as a consequence of agricultural activity (including excess application of inorganic nitrogenous fertilizers and manures), from wastewater disposal and from oxidation of nitrogenous waste products in human and animal excreta (WHO, 2011). The NO_3^- in the studied waters was possibly resulted from a consequence of agricultural activity. The waste products in human and animal excreta might also contribute to NO_3^- in the studied waters. However, currently detected NO_3^- in these waters are most probably due to the natural availability of NO_3^- in water because the current study was conducted during dry season which may not contribute to leaching of chemical fertilizers and animal manure. The average concentrations of NO_3^- (Table 5) in the studied waters varied between the minimum mean of 1.26 mg/L (Abba Nura) and the maximum mean of 32.2 mg/L (Mumme). Because of not industrialized area, the great differences in the concentrations of nitrate ions of Abba Nura and Chirecha might be due to a nitrogen occurs naturally in the soil in organic forms from decaying plant and animal residues that was converted to nitrate by bacteria, and leached to the study spring water. The obtained results are below the currently recommended guideline values for drinking water (Appendix I) indicating that no health problem associated with NO_3^- at the levels present in the investigated waters. One-way ANOVA test ($p = 0.05$) showed that the NO_3^- concentrations among the water springs are varied significantly owing to the differences in the movement of NO_3^- with ground water flow.

Phosphate (PO_4^{3-}): Water may contain PO_4^{3-} derived from natural contact with minerals or through pollution from application of fertilizer, sewage and industrial waste. Ground water, therefore, is more likely to have higher PO_4^{3-} concentration (Maiti, 2004). The PO_4^{3-} in the studied spring waters was possibly from the natural contact with minerals when the water bodies come across the layers of various minerals.The obtained results were varied between the minimum mean 0.07 mg/L in Abba Fasige Mumme and the maximum mean 0.34 mg/L in Chirecha (Table 5). Because phosphorus, as phosphates, is not deleterious to human health, guidelines like WHO and other national standards, do not typically list criteria for acceptable phosphorus concentrations for drinking water quality (Nollet, 2007). Also, currently no guideline value proposed by WHO and other national organizations for PO_4^{3-} in drinking water (Appendix I). The results of one-way ANOVA ($p = 0.05$) found that the PO_4^{3-} concentrations between the tested water springs varied considerably owing to the natural contact of these waters with PO_4^{3-}minerals which could be affected by the temperature of the

waters. High temperature is favorable for the release of phosphate by dissolving phosphate minerals.

4.5 AAS Analysis of Water Samples for Trace Metals

AAS was used for the analysis of selected heavy metals in water samples based on the principles of absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum by atoms resulting in changes in electronic structure, observed by passing radiation characteristic of a particular element through an atomic vapor of the sample. Samples are vaporized by aspiration of solution into a flame (Fifield and Kealey, 2000; Jeffery*et al*., 1989).

4.5.1 Method Validation and Quality Control Results

4.5.1.1 Detection Limits

To validate the analytical performance of the analysis the instrument detection limit, and method detection limit were determined for each of the analytes analyzed by instrumental methods

Table 7: **Detection Limits for water samples analysis.**

Technique	Analyte	IDL (mg/L)	Spike Level (mg/L)	MDL (mg/L)	10 x MDL (mg/L)	Recovery (%)	RSD (%)
Atomic Absorption Spectrophotometry	Ca	0.008	0.06	0.03	0.3	82.5	4.45
	Cd	0.004	0.02	0.016	0.16	83.98	9.71
	Cu	0.015	0.08	0.06	0.6	90.45	11.67
	Cr	0.03	0.2	0.12	1.2	91.09	14.35
	Zn	0.04	0.39	0.16	1.6	93.1	3.78

i. Instrument Detection Limits (IDL)

The determined IDL for each metal in water samples are given in Table 7. For Mn, and Cu, the IDL was determined through analysis of distilled water as calibration blank whereas for Cd, Cr and Zn the IDL was determined through analysis of 2% HNO_3 as calibration blank, respectively.

ii. Method Detection Limits (MDL)

The MDL of the analytical methods for each analyte were determined from six replicates of laboratory reagent spiked with the target analyte at a concentration four times the determined IDL of each analyte and calculated using equation (3.10). These calculated values (Table 7) represent the measured minimum concentration of the analytes and the values reported with 99 % confidence that the analyte concentration greater than zero.

The acceptability of the determined MDL was tested by comparing with the spike level, 10 times of calculated MDL, and also evaluated in terms of recovery and RSD. According to Wisconsin Laboratory Certification Program (1996), the following inequalities are useful for evaluating a calculated MDL:

Calculated MDL < Spike Level < 10 x Calculated MDL.

When we come across the calculated data (Table 7), these inequalities conditions are met verifying the acceptability of determined MDL. Also, the recovery and RSD of the calculated MDL are within the required limit: 80-120% for recovery and ≤ 20% for RSD (APHA, 1999). These show that the methods are well validated for the determination of the metals at trace amount.

4.5.1.2 Calibration curves

Calibration curves showing absorbance versus concentrations at a specific wavelength of each metal were constructed through analysis of the instrument blank and three point calibration standards for Cu and Mn, and four point calibration standards for Zn, Cd and Cr. As observed from calibration curves, the correlation coefficients (R^2) were varied between 0.999 and 1 which all are greater than the minimum acceptable value of 0.995 (APHA, 1999), showing that there was a good correlation between concentration and absorbance. The calibration curves are given in Appendix III.

4.5.2 Sample Analysis

The results for analyzed trace metals in water samples are given in Table 5.

Manganese (Mn): Mn concentrations were found between the minimum mean of 0.02 mg/L (Abba Fasige and Chirecha) and the maximum value of 0.13 mg/L (Mumme). All values are below the WHO and different national guideline values for drinking water quality (Appendix I).Therefore, no adverse effect concerned with Mn if waters are used for drinking purpose. One-way ANOVA (p = 0.05) showed that the Mn concentrations between water springs varied considerably which could be due to the variation in Mn minerals among the springs.

Cadmium (Cd): Cd concentrations in all studied spring waters were generally below the MDL (0.005 mg/L); therefore no substantial amount of Cd was detected in water samples.

The USEPA Primary Drinking Water Standard (2012) and Canadian Drinking Water Quality (2003) for Cd is < 0.005 mg/L. Therefore, no problem concerning with Cd in the waters for

drinking since the study results indicated that Cd concentration was <MDL.

Copper (Cu): As shown in Table 5, Cu concentrations in the investigated springs were found between the minimum mean of 0.039 mg/L (Abba Fasige) and the maximum mean of 0.07 mg/L (Abba Nura). According to WHO (2011), at levels above 5 mg/L, Cu imparts a color and an undesirable bitter taste to water. However, the detected values were below the WHO and different national guidelines for drinking water (Appendix I).Therefore, no health and aesthetic problems associated with Cu for drinking these waters. One-way ANOVA result ($p = 0.05$) showed that the Cu concentrations between the studied water springs varied considerably which could be due to the variation in Cu minerals among the springs.

Chromium (Cr): Like Cd, the Cr concentrations in the studied spring waters were also found to be below the MDL (0.05 mg/L) as indicated in Table 5. This indicates that the levels of Cr in these waters was not exceeded the maximum permissible value recommended by WHO and different national standards for drinking water quality (Appendix I). Therefore, no adverse effects concerning with Cr in these waters for drinking.

Iron (Fe): The obtained mean concentrations of Fe were found between the minimum mean concentration 0.03 mg/L (Abba Fasige) and the maximum mean concentration 0.147 mg/L (Mumme) (Table 5) and all are found to be below the recommended maximum value for drinking water (Appendix I). Therefore, all the water samples currently analyzed reveals that all have no adverse health effect and aesthetic problem concerned with Fe for drinking. One-way ANOVA result ($p = 0.05$) found that the Fe levels between the studied waters varied considerably owing to the variations in Fe minerals among the springs.

Zinc (Zn): The Zn concentrations were found between the minimum mean value 0.55 mg/L (Chirecha) and the maximum value of 0.704 mg/L (Abba Fasige). The Zn levels in the studied springs were below the WHO and different national guidelines for drinking water quality (Appendix I). Therefore, no adverse effects concerning with Zn in these waters for drinking. One-way ANOVA result ($p = 0.05$) showed that the Zn concentrations between the waters varied significantly which could be due to the variations of Zn minerals among the springs.

5. CONCLUSION AND RECOMMENDATIONS

Safe water is a precondition for health and development. Therefore, it necessitates knowing the quality of water for drinking. In this study, four densely populated spring waters (Abba Fasige, Mumme, Abba Nura, and Chirecha) of Hericha rural area, West Wollega, were analyzed for seven physico-chemical parameters (temperature, pH, EC, TDS, COD, TA, and TH); for eight major-chemical parameters (SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-, Ca, Mg, Na, and K) and six heavy metals (Mn, Cd, Cu, Cr, Fe, and Zn). During the study temperature, pH and EC were measured at site of sample collection. The COD, TA, TH, $^-$, Cl^-, Ca and Mg were determined by classical methods of analysis in laboratory. pH, PO_4^{3-}, NO_3^-, SO_4^{2-}, TDS, Na, K and heavy metals were determined by instrumental methods of analysis in laboratory.

All the analyses were carried out according to the procedures given in the standard methods (APHA, 1999). The obtained results of all the parameters were compared among the water springs. One-way ANOVA test ($p = 0.05$) showed that most of physico-chemical and major-chemical parameters varied significantly between the studied water springs. All the six trace metals analyzed except Cd and Cr, which are below method detection limit, were varied significantly between the studied water springs. The pH of all spring sites except the pH of Chirecha spring site, which is within the admissible limit, were below the range of WHO and different national guidelines (Appendix I). This indicates that the corrosive ability of water on the piping system is to some extent large. Even if the problem is not this much a great problem, it needs treatment because it is slightly acidic rather than normal water and thus must be reported for the issue it may concern (e.g. for the surrounding health office , water , woreda administration and the like). Among the six heavy metals Cd and Cr in water samples were below the MDL. From one-way ANOVA test ($p = 0.05$), all reported heavy metals varied significantly among the water springs.

The current study results were compared with WHO and different national guidelines for drinking water quality, and all analyzed parameters except pH were below the established guideline values. Therefore, no health and aesthetic problems concerning with the analyzed parameters of the waters for drinking. Generally, the importance of the quality of water for human consumption (regarding both health and aesthetic based quality) makes it necessary to investigate and keep up to norms, including limits for all the parameters that directly affect human health.

To conclude it is obvious that water is the first of all basic needs and its treatment is directly connected with value of human life. For this reason, the responsible organization and the woreda administration should work hand in hand to convince that the quality of water in Hericha should be assured. Therefore, it is recommended that further studies need to be done on heavy metals like Pb, Ni, etc, and the biological quality of the waters in order to improve the acceptability of the waters for drinking. It is also suggested that investigation of all recently studied and recommended parameters should be done on the other water springs in Hericha rural area in order to evaluate whether or not having any health risks concerned. The present study was conducted in the month between March and May which is partially dried season and partially summer season so that it is recommended to do the research in the remaining seasons of the year, mainly during completely summer season or completely dried season(the samples were collected two times within the ranges of these months).

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APPENDICES

AppendixI: Guidelines for Drinking Water Quality(for health risk and aesthetic value) set by different national and international organizations.

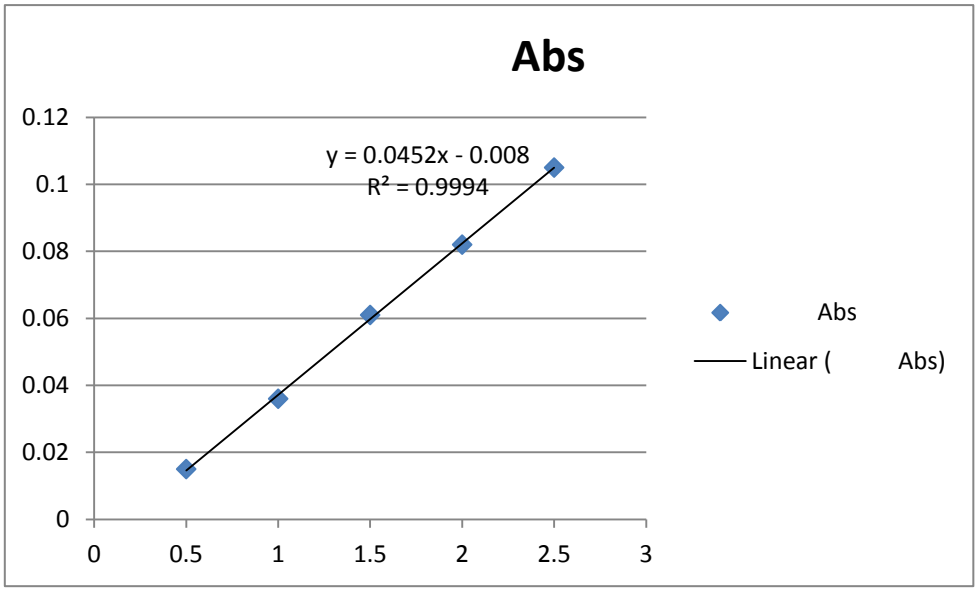
Parameter	Ethiopia, 2011	South Africa, 1996	USEPA, 2012	Pakistan, 2008	WHO, 2011	EEPA, 2003
Temperature (^oC)	NM[a]	NM	NM	NM	-	-
pH	6.5 - 8.5	6.0 - 9.0	6.5 - 8.5	6.5 – 8.5	6.5–8.5[b]	6-9
EC (µS/cm)	NM	700	NM	NM	-	1000
TDS (mg/L)	1000	450		1000	1000[b]	NM
COD (mg/L)	NM	NM	NM	10	NM	NM
TA (mg/L)	200	NM	NM	NM	NM	NM
TH (mg/L)	300	50 – 100	NM	< 500	200[b]	NM
NO_3^- (mg/L)	50	6.0	10	50	50	50
PO_4^{3-} (mg/L)	NM	NM	NM	NM	NM	NM
SO_4^{2-}(mg/L)	250	200	250 [b]	200	250[b]	200
Cl^- (mg/L)	250	200	250	<250	250[b]	250
Ca (mg/L)	75	32	-	75	NM	NM
Mg (mg/L)	50	30	250	50	NM	NM
Na (mg/L)	200	100	20	NM	200[b]	NM
K (mg/L)	1.5	50	NM	NM	NM	NM
Cu (mg/L)	2	1.0	1.3	2	2.0	0.112
Cr (mg/L)	0.05	0.05	0.1	0.05	0.05	0.05
Cd (mg/L)	0.003	0.005	0.005	0.01	0.003	0.005
Zn (mg/L)	5.0	3.0	5.0 [b]	5.0	5.0[b]	0.5
Mn (mg/L)	0.5	0.05	0.05	0.5	0.4	0.3
Fe (mg/L)	0.3	0.1	0.3	0.3	0.3[b]	1.0

[a] NM: Not Mentioned.

[b] Aesthetic Based Value.

Appendix II: Spectrophotometric standard calibration curve for NO_3^-, PO_4^{3-}.and SO_4^{2-}

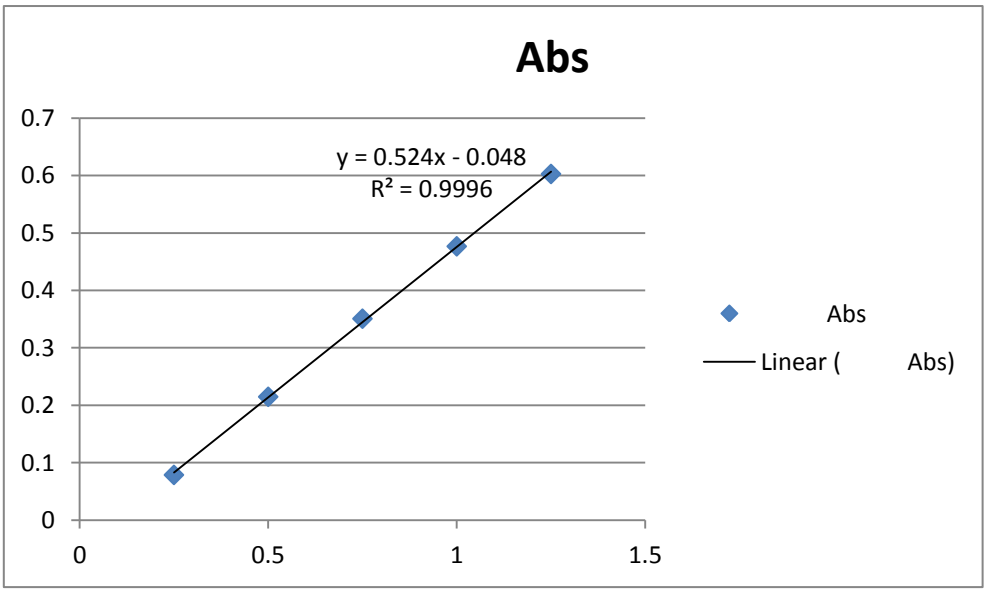
Calibration curve for NO_3^-



A B S

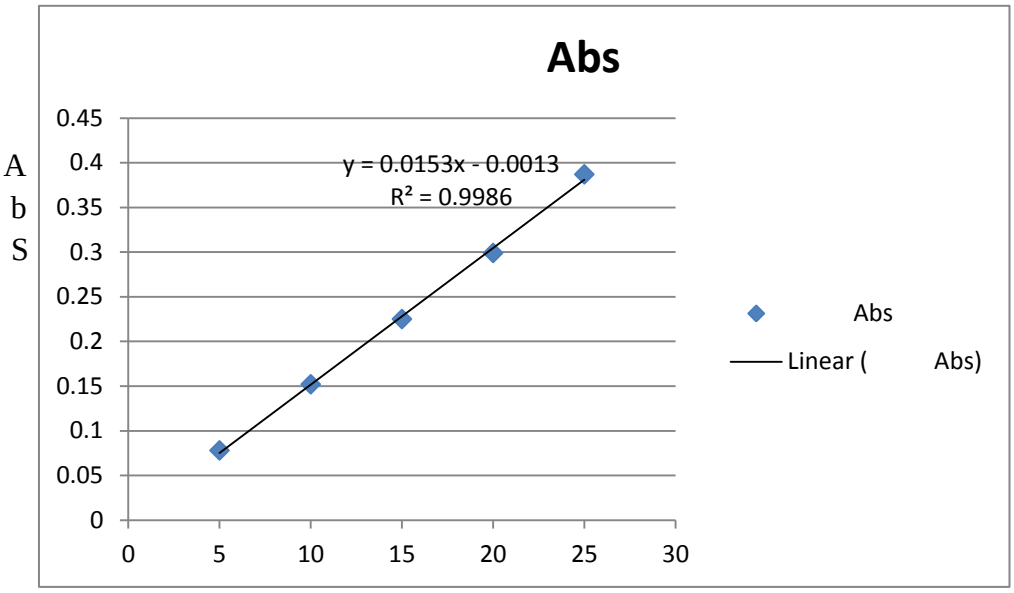
Conc.(mg/L)

Calibration Curve for PO_4^{3-}



A b S

Calibration Curve for SO_4^{2-}

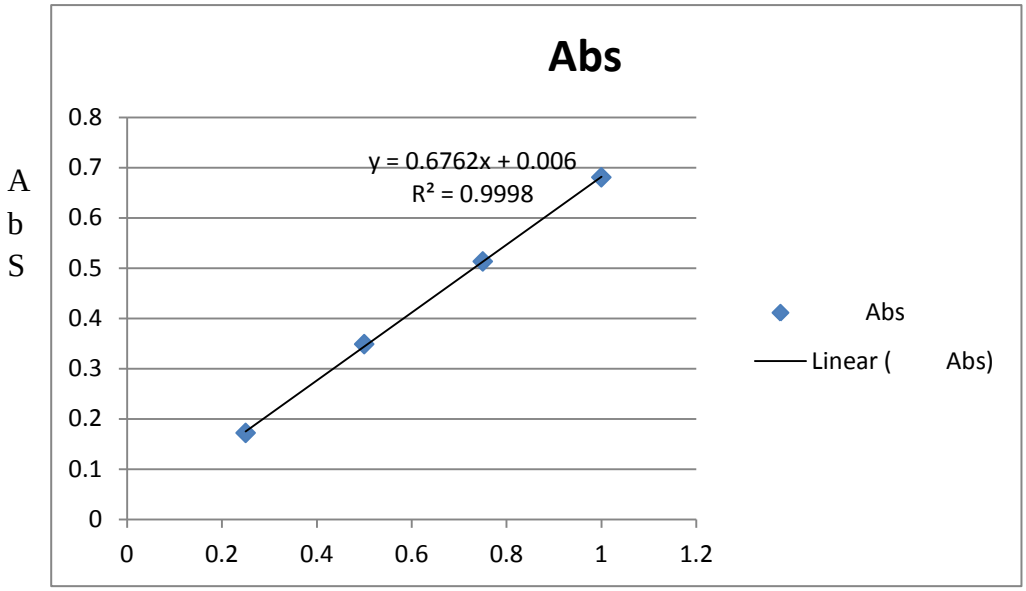


A
b
S

Conc.(mg/L)

Appendix III: AAS Spectrophotometric calibration curve for the determined heavy metals.

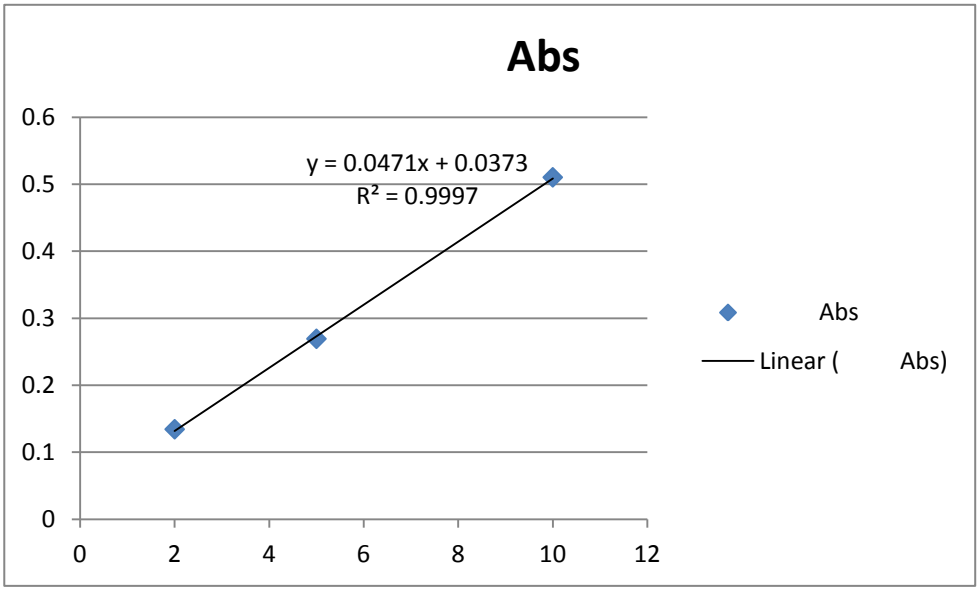
Calibration Curve for Zn



A
b
S

Conc.(mg/L)

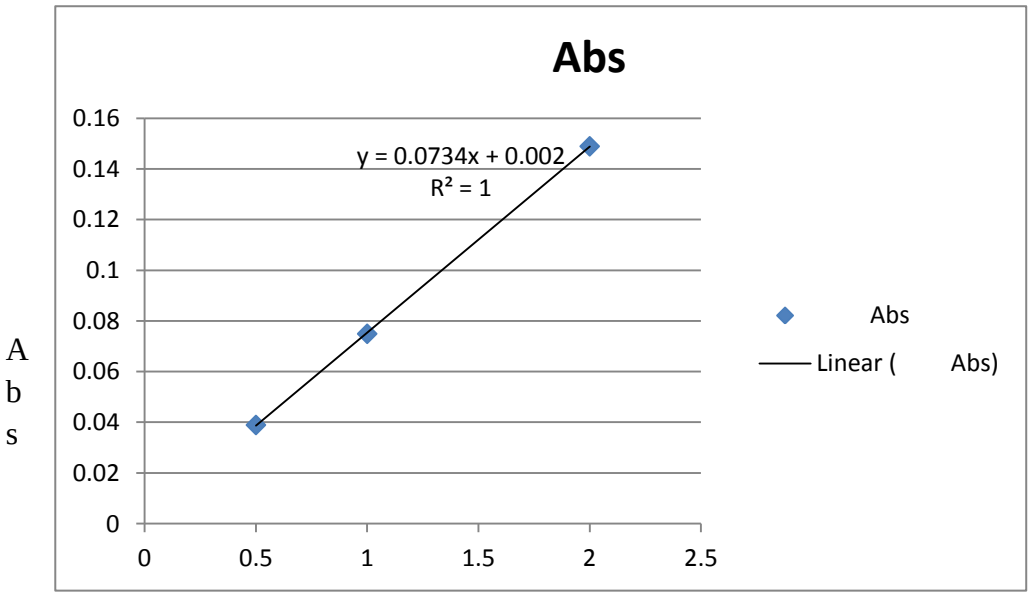
Calibration curve for Mn



A
b
S

Conc.(mg/L)

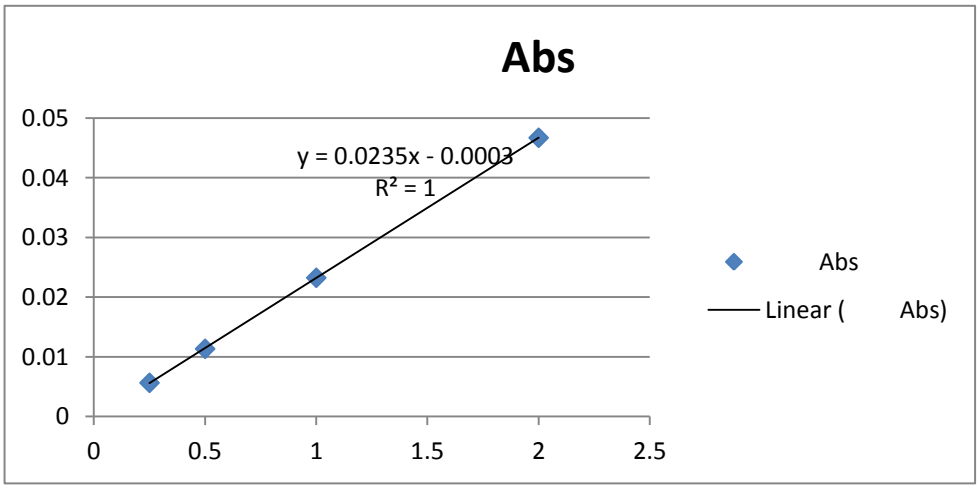
Calibration curve for Cu



Abs

Conc.(mg/L)

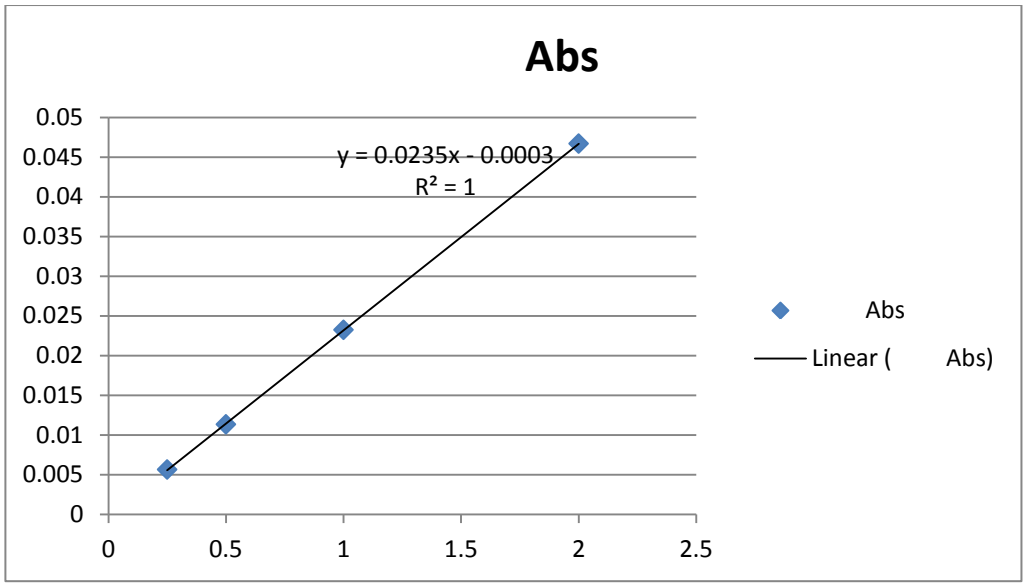
Calibration Curve for Cr



Abs

Conc.(mg/L)

Calibration curve for Cd



A

B

S

Conc.(mg/L)