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DETERMINATION OF QUALITY OF SPRINGS AND DEEP WELL WATER CONSUMED IN JIBAT-SHENEN DISTRICT OF WEST SHOA, OROMIYA STATE, ETHIOPIA.

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR MASTER OF SCIENCE DEGREE IN ANALYTICAL CHEMISTRY

M.Sc. Thesis

By Dinaol Merera

August, 2015

Adama, Ethiopia

DETERMINATION OF QUALITY OF SPRINGS AND DEEP WELL WATERS CONSUMED IN JIBAT-SHENEN DISTRICT OF WEST SHOA, OROMIYA STATE, ETHIOPIA.

M.Sc. Thesis

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY.

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August, 2015

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ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

SCHOOL OF GRADUATE STUDIES

As members of examining board of the Final M.Sc. Thesis Open Defense, we certify that we have read and evaluated the Thesis entitled “Determination of Quality of Spring and Deep well water Consumed in Jibat-Shenen District of West Shoa, Oromiya State, Ethiopia” is prepared by Dinaol Merera Kumsa and examined the candidate. We recommended that the Thesis be accepted as fulfilling the Thesis requirement for the Degree of Master of Science in Analytical Chemistry.

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I certified that this work entitled with "Determination of Quality of Spring and Deep Well Water Consumed in Jibat-Shenen District of West Shoa Oromiya State, Ethiopia" was done independently by Dinaol Merera Kumsa under my guidance and supervision and that it has not previously formed the basis for the award of any fellowship or associated ship.

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DECLARATION

I sincerely and solemnly declare that the research conducted in fulfillment of the requirement of the degree of Master of Science in Analytical Chemistry to the School of Graduate Studies of Adama science and technology University entitled "Determination of Quality of Spring and Deep Well Water Consumed in Jibat-Shenen District of West Shoa Oromiya State, Ethiopia" is my own work and that all sources that I have used or quoted have been indicated and acknowledged by means of references and also that this thesis was not previously to any other institution/university anywhere for award of academic degree/diploma.

Dinaol Merera Kumsa	_____	_____	_____
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This is to certify that the thesis prepared by **Dinaol Merera**, entitled **"Determination of Quality of Spring and Deep Well Water Consumed in Jibat-Shenen District of West Shoa Oromiya State, Ethiopia**" and submitted in fulfillment of the requirement for the Degree of Master of Science in Chemistry complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

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LISTS OF ACRONYMS AND ABBREVIATIONS

A. R.	Analytical reagent
AAS	Atomic Absorption spectrometer
BMDL	Below method detection limit
DO	Dissolved Oxygen
E S	Ethiopian Standards
EBT	Eriochrome Black-T
EC	Electrical conductivity
EDTA	Ethylene Diamine tetra acetic acid
EPA	Environmental Protection Agency
FAAS	Flame Atomic Absorption Spectroscopy
FAO	Food and Agricultural Organization
FAS	Ferrous ammonium sulfate
FDA	Food and Drug Agency
FDRE	Federal Democratic Republic of Ethiopia
IDL	Instrument Detection Limit
IUPAC	International Union of Pure and Applied Chemistry
LR	Laboratory reagent
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
NE	North East
ppm	parts per million
RPD	Relative percent difference

RSD	Relative standard deviation
SW	South West
TA	Total Alkalinity
TDS	Total Dissolved Solids
TH	Total Hardness
UD	Undetected
USEPA	United State Environmental Protection Agency
UTM	Universal Time Measure
UV-Vis	Ultraviolet-visible spectroscopy
WHO	World Health Organization

Abstract

The present study was conducted to assess and clarify concerns about quality and safety of drinking spring and deep well water in Jibat-Shenen district of Oromiya state. Water samples were collected from 2 densely populated springs and one deep well of the area, namely: Laga Sose, Abba Moga and Laga Dada, respectively. All the samples were analyzed for six physico-chemical parameters (temperature, pH, total dissolved solids, conductivity, alkalinity, hardness); four Common cations (Ca, Mg, Na ,K) ; four common anions (SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl); and three toxic heavy metals (Cd, Cr, and Pb) using standard methods. Temperature, pH and Electrical conductivity were measured in situ at the study site; DO was analyzed by titrimetric procedure using the azide modification of Winkler method. Alkalinity, hardness, SO_4^{2-}, Cl^-, Ca and Mg were determined by classical methods. PO_4^{3-}, NO_3^-, Na, K and heavy metals were analyzed by instrumental methods i.e. K and Na were analysed using flame photometry; Ca and Mg were determined titrimetrically; SO_4^{2-} and NO_3^- concentrations were investigated by using UV-Vis spectrophotometer. Chloride was determined by argentometric titration which is a direct titration of Cl^- available in the water sample by standard Ag^+(0.1N) using CrO_4^{2-}as an indicator; Hardness is determined by the EDTA method in alkaline condition and Alkalinity was determined by titration using indicators (phenolphthalein and methyl orange indicators). The metal analysis was done by FAAS to detect cadmium, chromium, and lead. The in-situ measurements showed that mean values of temperature, pH, and conductivity were ranged from 20.85 to 23.27 ^oC, 6.67 to 8.2 and 27.80 to 47.10µS/cm, respectively. The mean results for TDS, alkalinity, hardness and DO were varied from 18.00 to 32.90 mg/L, 5.76 to 7.20 mg/L, 18.80 to 27.60 mg/L, and 9.140 to 22.043 mg/L, respectively. The major chemical analysis showed that the mean values ranged from 0.009 to 0.015 for PO_4^{3-}, 1.975 to 9.548 for NO_3^-, 3.10 to 4.10 for Cl^-, 1.45 to 2.23 for Mg , 5.13 to 7.37 for Ca, 0.333 to 7.067 for K, 5.567 to 21.833 for Na. Among the three heavy metals analyzed for waters Cd and Cr were below the method detection limit. However, the concentration of Pb was 0.3 mg/L in laga abba moggaa spring water and 0.5 mg/L in laga Dada deep well. SO_4^{2-} was undetected in all samples.

Key words: *Spring and deep well water, heavy metals, physico-chemical properties and spectroscopy.*

CHAPTER ONE

1 INTRODUCTION

1.1 Background of the study

Any society those considering the provision of safe drinking water a priority are considered as civilized societies. This is because safe drinking water is a basic need to human development, health and well-being. Water covers almost 75% of the earth's surface. The quantity and the quality of water are equally important. The quality of water used for drinking, domestic purpose, food production or recreational purposes have an important impact on health (WHO, 2013). Water is a dynamic system containing living as well as non-living, organic, inorganic, soluble as well as insoluble substances. Various health problems may occur due to inadequacy and poor quality of water supply. Water is always referred to as a universal solvent because it can dissolve many types of substances, but human require water that contains less impurities. The ensuring of good quality drinking water is a basic factor in guaranteeing public health, the protection of the environment and sustainable development (Ranjini et al., 2010). Water of good drinking quality is of basic importance to human physiology and man's continued existence depends very much on its availability (Lemikanra, 1999).

Water can be obtained from a number of sources, among which are streams, lakes, rivers, ponds, rain, springs and wells (Okonko et al., 2008). In Ethiopia, the dominant source of drinking water used to supply major urban and rural communities is from wells and springs. Unfortunately, clean, pure and safe water can exist only briefly in nature and immediately polluted by prevailing environmental factors aided by human activities. Water from most sources is therefore unfit for immediate consumption without some sort of treatment (Okonko et al., 2008).

Although there are no 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 (Gebrekidan and Samuel, 2011). A drinking-water quality guideline value represents the concentration of a constituent that does not result in any significant health risk to the consumer over a lifetime of consumption. Drinking-water should be suitable for human consumption and for all usual domestic purposes (WHO, 1997). The quality of water in any environment provides significant information about the available resources for supporting life in that environment. It is difficult to imagine clean and sanitary environment without water. Without safe drinking water communities also cannot be healthy (WHO, 2011).

The primary aim of the WHO Guidelines for Drinking-water Quality (GDWQ) is the protection of public health. As WHO Guidelines for Drinking-water Quality (WHO, 2010) recommends, the quality of drinking water is a powerful environmental determinant of health.

Thus, the present study was undertaken with the objective to assess the quality of spring and deep well water consumed in Jibat Shenen District of Oromiya State.

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).

An abundant supply of clean and safe drinking water is essential for human and animal health. But in nature, all water contains some impurities. As water flows in streams, accumulates in lakes and filters through the layers of soil and rock in the ground, it dissolves and absorbs the substance that come in contact with it. Some of these substances are harmful and others are harmless. However, at certain level, minerals may consider contaminants that can make water unpalatable or even unsafe. Lack of access to safe and clean water is locked in the heart of the poverty. These substances can be result of human activities or can be found in nature.

Spring and deep well waters are the main sources of drinking water in the rural and most urban settlements of Ethiopia. Spring water is a surface water source and Deep wells are drilled wells with electric pumps that seldom used as drinking water.

Thus, the spring water and deep well water are one of the parts of earth's surface used for drinking that should be identified either with expected limiting value or not in the studied areas.

1.3 Research Objectives

1.3.1 General Objective

The main intention of this research is to determine the physico-chemical parameters of environmental indicators, the level of common cations and anions and some heavy metals in spring and deep well water in order to study the safety level of using spring and deep well water in Jibat-Shenen District, Oromiya State of Ethiopia.

1.3.2 Specific Objectives of the Study

The specific objectives of the study were:

- To determine the selected physico-chemical properties of environmental indicators (temperature, pH, EC, TDS, DO, TA, and TH) of Jibat Shenen district springs and deep well water.
- To determine the level of common cations (Ca, Mg, Na and K), anions (SO_4^{2-}, PO_4^{3-}, NO_3^- and Cl^-) and some toxic heavy metals (Pb, Cd, Cr) in springs and deep well water by Flame photometry, UV-vis and FAAS, respectively.
- To compare some parameters of spring water with deep well water to ensure their quality comparing with recommended limit given to water quality.
- To compare the results with the national and international standard of water quality for drinking according to standards given by US EPA, WHO and ES.

1.4 Significance of the Study

It is very important to know the quality of water we drink for our health. Some scholars have tried to assess the quality of drinking water in Ethiopia. Assessment in the district and comparing mineral contents of water used for drinking in district with accepted standards of water guidelines is also very important. Thus, this study is expected to give the baseline information about spring and deep well water quality in Jibat Shenen rural area regarding the selected physico-chemical environmental indicators, some common ions and some toxic heavy metals. Moreover, the study outcome will provide information about the acceptability of the waters for drinking by comparing with drinking water quality standards given by national and international agency. This study also can provide some information for those who are interested in conducting further study and can create awareness among the local people about their water quality standards that they use in different activities and can help government organization and Non-Government organization to assess their water quality.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 Spring and Deep well water

Spring water occurs wherever ground water flows out from the earth's surface that formed when natural pressure forces ground water above the land surface. It is 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 the water is considered safe for drinking. Testing helps to determine exactly how much treatment is necessary and may help determine if other sources of water would be more economical (Geyikçi *et al.*, 2012; Lawson, 2011).

Deep wells are drilled wells with electric pumps that can get water from a much deeper level by mechanical drilling and are currently used throughout the world, typically in rural or sparsely populated areas.

2.2 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, DO, total dissolved solids (TDS), hydrogen ion concentration (measured as pH), alkalinity and hardness (Weiner, 2008; USEPA, 2006).

2.2.1 Temperature

Temperature is an important biologically significant factor, which plays an important role in the metabolic activities of the organism. The temperature of water can affect it in many different ways. 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). When the temperature goes up, water will hold more dissolved solids (like salt or sugar) but less dissolved oxygen. The opposite is true for colder water that contains more oxygen, which is better for animal life like fish and insect larvae (WHO, 2011).

2.2.2 Electrical Conductivity

Electrical conductivity (EC) is a measure of water capability to transmit electric current and depends upon the number of ions or charged particles in the water to assess the purity of water. It signifies the amount of total dissolved salts (Gopalkrushna et.al, 2011). Most dissolved inorganic substances in water are in the ionized form and hence contribute to conductance. EC 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 water ways where plant nutrients (fertilizer) are in greater abundance. Very high values are good indicators of possible polluted sites. The conductivity of the water should be less than 1 µmhos/cm (APHA, 1999).

2.2.3 Total Dissolved Solids (TDS)

Total dissolved solids (TDS) comprise inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates) and some small amounts of organic matter (material) that are completely dissolved in water (WHO, 2011, Ethiopian Water Technology Centre, 2008). TDS in drinking-water originates from natural sources, sewage, urban runoff and industrial wastewater. Salts used for road de-icing in some countries may also contribute to the TDS content of drinking-water. Concentrations of TDS in water vary considerably in different geological regions owing to differences in the solubilities of minerals. 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). The WHO concludes the preferable level of TDS in water as shown in Table 1.

Table 1: The preferable level of TDS in water as studied by WHO.

Level of TDS (mg/L)	Rating
Less than 300	Excellent
300-600	Good
600-900	Fair
900-1,200	Poor
Above 1,200	Unacceptable

2.2.4 pH

The pH level is the measurement of the activity of the hydrogen atom because the hydrogen activity is a good representation of the acidity or alkalinity of the water. Water with a low pH is said to be acidic and water with a high pH is basic or alkaline. Pure water would have a pH of 7.0. Most of the water supplies are slightly alkaline due to presence of carbonates and bicarbonates. pH of most natural water falls within the range of 4 to 9. The higher range of pH indicates higher productivity of water causing taste, soapy feel, and the lower pH causes corrosion. WHO prescribed preferably, pH <8.0 is preferable for effective disinfection with chlorine (S. K. Maiti, 2004). The pH increases during daytime due to photosynthetic activity because of consumption of CO_2, where as it declines at night due to respiratory activity. 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).

2.2.5 Dissolved Oxygen (DO)

Dissolved Oxygen (DO) is important parameter in water quality assessment and reflects the physical and biological processes prevailing in the water. DO analysis measures the amount of gaseous oxygen (O_2) dissolved in aqueous solution and its values indicate the degree of pollution in water bodies. Oxygen gets in to water by diffusion from the surrounding air, by aeration (rapid movement) and as west product of photosynthesis. The solubility of atmospheric oxygen in fresh water ranges from 14.6mg/L at 0°C to about 7.0mg/L at 35°C under normal atmospheric pressure. Since it is poorly soluble gas, its solubility directly varies with the atmospheric pressure at any given temperature.

When only parts of the sample of the content are titrated, i.e. 100 or 250 mL.

$$\text{DO in mg/L} = \frac{\text{mL of titrant x Normality x 8 x 1000}}{\text{V}_2\ (V_1 - \text{v})/V_1} \quad \ldots\ldots (2.1)$$

Where, V_1=Volume of BOD bottle, mL, V_2=Volume of the contents titrated, mL and v = Volume of $MnSO_4$ and iodide azide added, i.e. 1 + 1 = 2 mL

2.2.6 Alkalinity

Alkalinity (AT) is the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. It is a measure of the water ability to absorbed H^+ without significant pH change. It is the sum of all the titrable bases. Alkalinity of sample can be estimated by titrating with standard sulphuric acid (0.02N) at room temperature using phenolphthalein and methyl orange indicator. 'Phenolphthalein alkalinity' is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination (APHA,1999). The major portion of alkalinity in natural waters is caused by hydroxide, carbonate, and bicarbonate (S.K. Maiti, 2004). 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 = $\frac{(C \text{ x } N)\text{x } 50 \text{ x } 1000mL}{V}$……..……(2.2)

Total alkalinity, (mg $CaCO_3$)/L = $\frac{(C+D)\text{x N x } 50 \text{ x } 1000\text{mL}}{\text{V}}$……..……..…….(2.3)

Where, C = the volume in mL of HCl solution used to reach pH = 8.3, D= the volume in mL of HCl solution used to reach pH = 4.4, N= the concentration of standard HCl solution in normality, V= the volume of sample in mL, 50=Equivalent weight of $CaCO_3$ (Zhang, 2007; Weiner, 2008).

2.2.7 Total Hardness

Hardness is defined as the concentration of multivalent metallic cations in solution that mainly depends upon the amounts of calcium or magnesium salts or both which precipitate soap scum and the need for excess use of soap to achieve cleaning. The hardness of water reflects the nature of geological formation with which it has been in contact (S.K. Maiti, 2004). Hard water are generally considered to be those waters that requires considerable amounts of soap to produce a foam /lather/ and that also produce scale in hot-water pipes, heaters, boilers and other units in which the temperature of the water is increased. The degree of hardness becomes greater as the calcium and magnesium content increases. Total hardness is defined as the sum of the calcium and magnesium concentration, both expressed as $CaCO_3$, in mg/L. The degree of hardness of drinking water has been classified in terms of the equivalent $CaCO_3$ concentration as shown in Table 2. Hardness is estimated titrimetrically.

Total hardness (as $CaCO_3$ mg/L) = $\frac{\text{A X B X } 1000}{mL \, of \, sample}$ … … … … … … … … … … … … … … … . … …(2.4)

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/0.01M EDTA used/ (APHA, 1999).

Table 2: Classification of hard water in terms of degree of hardness

Hardnessrange *(mg/L* as $CaCO_3$)	Degree of hardness
0-75	Soft
75-150	moderately hard
150-300	Hard
Above 300	Very hard

Ca- Hardness: Calcium and magnesium are common constituents of natural water and important contributor to the hardness of water. The source of Ca and Mg is the rocks from which it is leached. Being an important contributor of hardness, it reduces the utility of water for domestic use. Some $CaCO_3$ is desirable for domestic water because it provides a coating in the pipes which protects them against corrosion.

$$\text{Calcium hardness as mg of } CaCO_3/L = \frac{A \times B \times M \times 1000}{\text{Volume of sample(mL)}} \quad \text{.....(2.5)}$$

Where, A -Volume of EDTA consumed in titration, B -mg $CaCO_3$ equivalent to 1mL EDTA titrant, M - Concentration of EDTA

Mg-Hardness: Magnesium has been considered as non-toxic to humans at the concentration expected in water. Magnesium salts have a laxative and diuretic effect particularly for individuals not accustoms to high dosage. Magnesium hardness can be obtained by subtracting Ca-hardness from total hardness.

Mg hardness as $CaCO_3$ = Total hardness as $CaCO_3$ - Ca hardness as $CaCO_3$

Magnesium, mg/L= (TH as mg $CaCO_3$/L - Calcium Hardness as mg $CaCO_3$/L) x 0.243..... (2.6)

Where, TH = Total Hardness, mg $CaCO_3$/L.

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. It is usually caused by the presence of calcium and magnesium sulfates and/or chlorides in the water, which become more soluble as the temperature rises. There is no water hardness standard from EPA, but as given in Table 3, the Water Quality Association (WQA) has established the water hardness standards (Ideris, 2008).

Table 3: **The Measurement for Water Hardness by Water Quality Association (WQA)**

Hardness Level	Gpg	mg/L or ppm
Soft	less than 1.0	less than 17.1
Slightly Hard	1.0 to 3.5	17.1 to 60
Moderately Hard	3.5 to 7.0	60 to 120
Hard	7.0 to 10.5	120 to 180
Very Hard	10.5 and above	180 and above

(Adapted from Zafifi Bin Ideris, 2008).

2.3 Major Chemical Parameters

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

2.3.1 Calcium and Magnesium

Calcium (Ca): Ca is an essential nutrient for plants and animals which are 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 non-toxic. 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).

2.3.2 Sodium and Potassium

Sodium (Na): 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 water, 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). It occurs widely in the environment, including all natural waters. 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. 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).

2.3.3 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). The Cl^- ion was determined by argentometric method and calculated according to the following formula (APHA, 1999):

$$Cl^- \text{ (in mg/L)} = \frac{(A-B)X\ N\ X\ 35{,}450}{\text{Volume (mL) of samples}} \quad \text{..... (2.7)}$$

Where: *A* = mL titration for sample *B* = mL titration for blank, and *N* = normality of 0.0141*N* $AgNO_3$ (APHA, 1999).

2.3.4 Nitrates

Nitrate is the most highly oxidised form of nitrogen compounds commonly present in natural waters (APHA, 1999). Significant sources of nitrate are chemical fertilizers, decayed vegetable and animal matter, domestic effluents, sewage sludge disposal to land, industrial discharge, leachates from refuse dumps and atmospheric washout. Excessive concentration in drinking water is considered hazardous for infants (blue baby syndrome because of their small total blood volume) because of its reduction to nitrite in intestinal track causing methemoglobinaemia which result from oxygen deficiency. In surface water, nitrate is a nutrient taken up by plants and converted into cell protein. The growth stimulation of plants, especially of algae may cause objectionable eutrophication. 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).

2.3.5 Phosphates

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).

2.3.6 Sulphates (SO_4^{2-})

Sulphate is one of the major anions occurring in natural waters (S.K. Maiti, 2004). The highest concentrations are usually found in groundwater and expected to atmospheric deposition, industrial runoff, and natural sources such as gypsum ($CaSO_4.\ 2H_2O$) and anhydrite ($CaSO_4$) (Saadeh, 2012). SO_4^{2-} ions are discharged into surface water through industrial wastes and atmospheric deposition of

SO_2 (USEPA, 2008). The SO_4^{2-} is determined by Uv-Visible spectrophotometry and calculated using the following formula (APHA, 1999):

$$SO_4^{2-} \text{ (in mg/L)} = \frac{\text{mg BaSO4 X 411.6}}{\text{Volume (mL) of sample}} \quad \text{..... (2.8)}$$

2.4 Heavy Metals

Heavy metals are elements with high atomic weights that are generally toxic in relatively low concentrations to plant and animal life. They 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).

2.4.1 Some Selected Heavy Metals (Cr, Cd and Pb)

Chromium (Cr): Chromium is found chiefly in chome-iron ore or chromite ($FeCr_2O_2$). Chromium is used in alloys, in electroplating and in pigment. Chromium salts are used extensively in industrial processes and may enter a water supply through the discharge of wastes. Chromate compounds frequently are added to cooling water for corrosion control. Chromium may exist in water supplies in both the hexavalent and the trivalents state although the trivalent form rarely occurs in potable water. USEPA drinking water standard for chromium is 0.1mg/L. WHO (2011) recommended a MCL of 0.05 mg/L as a total concentration of Cr for drinking water.

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.

Cadmium (Cd): Cd is usually present in all soils and rocks that often released during volcanic action. These deposits can serve as sources to ground and surface waters, especially when in contact with soft, acidic waters. Average concentrations of Cd in U.S. waters are about 0.001 mg/L.

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.

Lead (**Pb**): Lead is nonessential for plants and animals. Lead in a water supply may come from industrial, mine, and smelter discharges or from the dissolution of plumbing and plumbing mixtures (APHA, 1999). Industrial and mining sources may contribute to some localized Pb pollution. Use of Pb pipes in water supplies may provide high Pb at consumers' points (S. K. Maiti, 2004). The international public health associations have reduced the permitted amount of lead in drinking water. For example, the European Community (EC) recommends a limit of 50 µg/L of lead in potable waters, which requires a method of lead determination with sensitivity much higher than that offered by conventional flame atomic absorption spectrometry.

Health Concerns of Pb: Lead is a toxic heavy metal and can affect many organs in the human body. Prolonged intake of even low concentrations of lead can cause serious problems for human health. The health effects of Pb are neurotoxic and three human systems are most affected: blood-forming system, nervous system (which include irreversible brain damage) and renal system. Such a toxic level is reached when the blood level exceeds 100-120 µg/L (S. K. Maiti, 2004). The Food and Drug Administration regulates lead content in food and in house paints. Under the lead-copper rule, the U.S. EPA drinking water 90th percentile action level is 15µg/L (APHA, 1999).

2.4.2 Flame Atomic Absorption Spectrophotometric Analysis of Heavy Metals

2.4.2.1 Principles of FAAS

The basic principle of flame atomic absorption spectroscopy is that: a liquid sample is aspirated and mixed as an aerosol with combustible gasses (acetylene and air in this particular study). The mixture is ignited in a flame and during combustion; atoms of the element of interest in the sample are reduced to the atomic state. A light beam from a lamp whose cathode is made of the element being determined is passed through the flame into a monochronometer and detector. Free, unexcited ground state atoms of the element absorb light at characteristic wavelengths; this reduction of the light energy at the analytical wavelength is a measure of the amount of the element in the sample (Beaty and Kerber, 1993; Harris,

2010). 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).

Quantification in AAS is usually done through external calibration. In this method the absorbance of standard solutions containing known concentrations of analyte are measured and the absorbance data are plotted against concentration to establish a calibration curve. After such a calibration is developed, the absorbance of solutions of unknown concentrations is measured and their concentrations are determined from the corresponding regression line equations by using the following general equation (Beaty and Kerber, 1993):

$$Y = mX + b \quad \text{(2.9)}$$

Where: 'Y' is the signal (absorbance); 'm' is slope of the regression line; 'X' is concentration and 'b' is the y-intercept.

2.4.2.2 Digestion Methods for Heavy Metal Analysis

Samples to be analyzed for metal content are usually prepared by digesting the matrix in a strong acid. Nitric acid is commonly used, because there is no chance of forming insoluble salts as might happen with HCl or H_2SO_4 and it yields a clear solution containing the metals for analysis by AAS techniques. Wet digestion with oxidizing acids is the most common sample preparation procedure and a method of converting the components of a matrix into simple chemical forms that produced by supplying energy, such as heat; by using a chemical reagent, such as acids (HNO_3/HCl). It has the advantage of being effective on both inorganic and organic materials and often destroys or removes the sample matrix, thus helping to reduce or eliminate some types of interference (Mester and Sturgeon, 2003; Barcelo, 2000). The relatively clean water sample such as groundwater or the tap water sample does not require acid digestion (Zhang, 2007).

2.4.3 UV-Vis Spectrophotometer

UV/Vis spectroscopy is an important analytical technique in modern water analysis. Many cations and anions in water can be determined with high selectivity and sensitivity.

3. MATERIALS AND METHODS

3.1 Description of study area

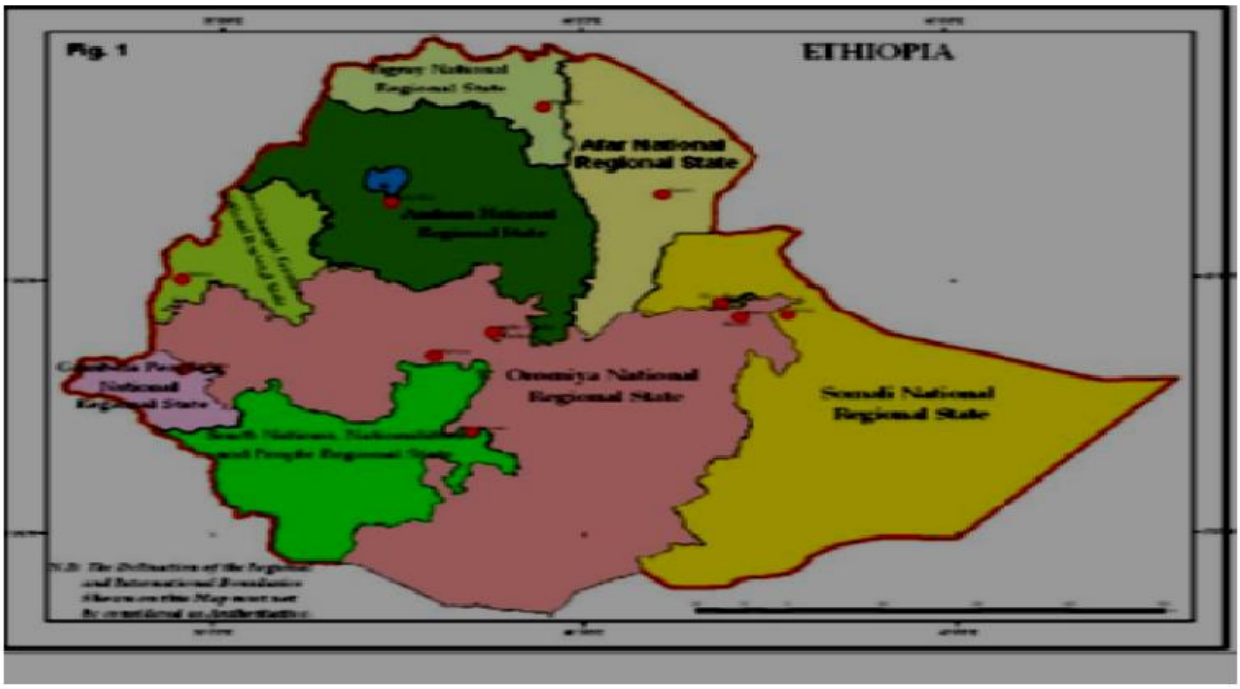
The study area is situated in Shenen community of Jibat district in the western part of Oromiya regional state, Ethiopia. Jibat is one of the woreda found in west shoa zone of Oromiya regional state, at a total distance of 184 km from capital city of Ethiopia, Addis Ababa to the west and 70 km from capital of zone, Ambo. The district is bounded by district Nono in the south, Danno in the west, Cheliya in the North West, Tikur Inchini in the east, Toke kutaye in the north-east and Ameya in south-east. Astronomically, the selected site is located between grids of 8^0 18' 0.5" N and 8^0 54' 00" N latitude and 37^0 17' 00" E in UTM and 37^0 38' 00" E longitude and its total area is 504.30 km^2.

The altitudinal range of the district above sea level is 1600-3200 meters with annual average rain fall 850-1450mm and the annual average temperature is 10^oC -25^oC. Naturally, the district characterized by three agro-climatic zones (Traditional thermal zones) namely cool Temperate (Baddaa) (47.83%), Temperate (Badda-Daree) (45.65%) and Hot zone (Kolla) (Gammoojjii) (West shoa zone, 2003 E.C).

There are several springs in surrounding area for instance Burqa Abba Mogga, Asnake, laga Ashetu and Laga sose springs are the dominant springs found in the surrounding area. Shenen town known for its good ground water potential. Under Jibat Mountain, there is several springs flow NE to SW. Recently in 2005 E.C. one deep well of anticipated depth of **132m**, named is "Laga Daadaa" is recommended to alleviate the drinking water problem of the Shenen and surrounding community.

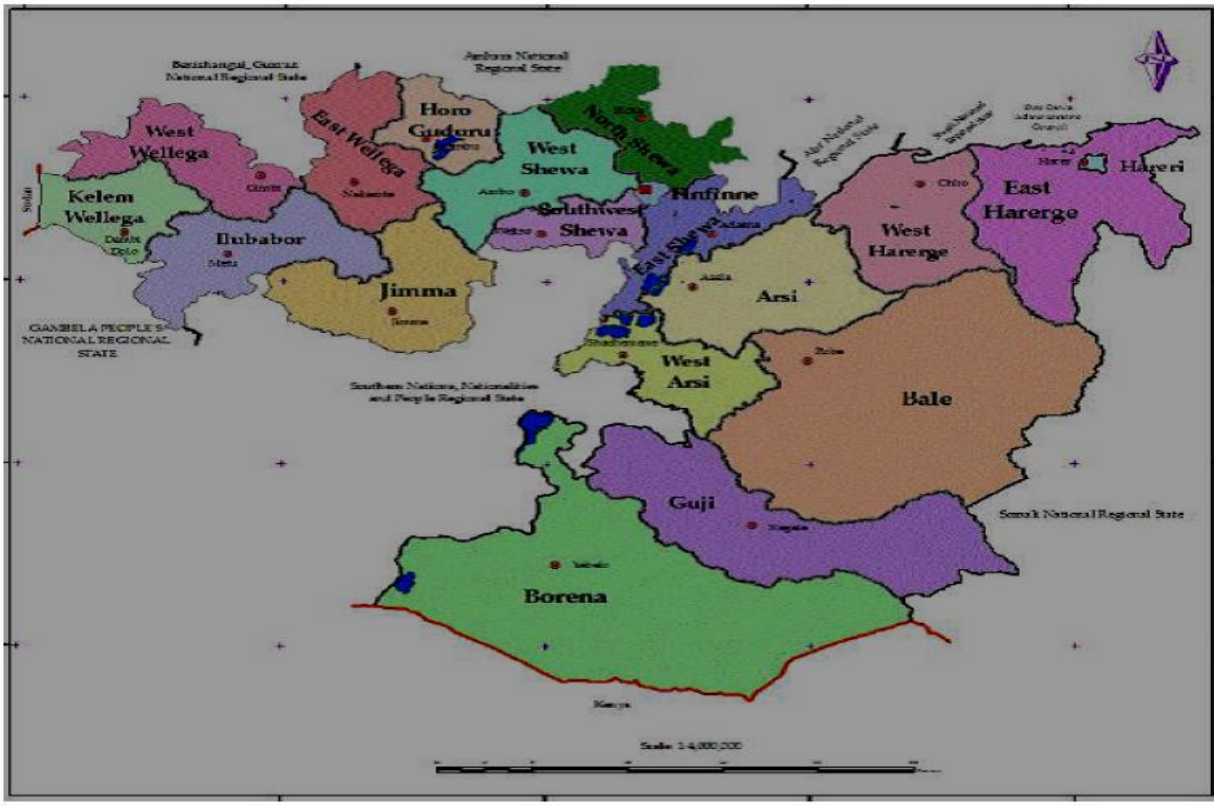
Thus, to estimate the quality of the water consumed in Jibat-Shenen district of Oromiya state the 2 spring waters and 1 deep well water samples were collected from three different locations. The details of sampling locations have been summarized in Figures 3.1, 3.2, 3.3 and 3.4.

Figure 3.1. Location of Oromia Region in Ethiopia



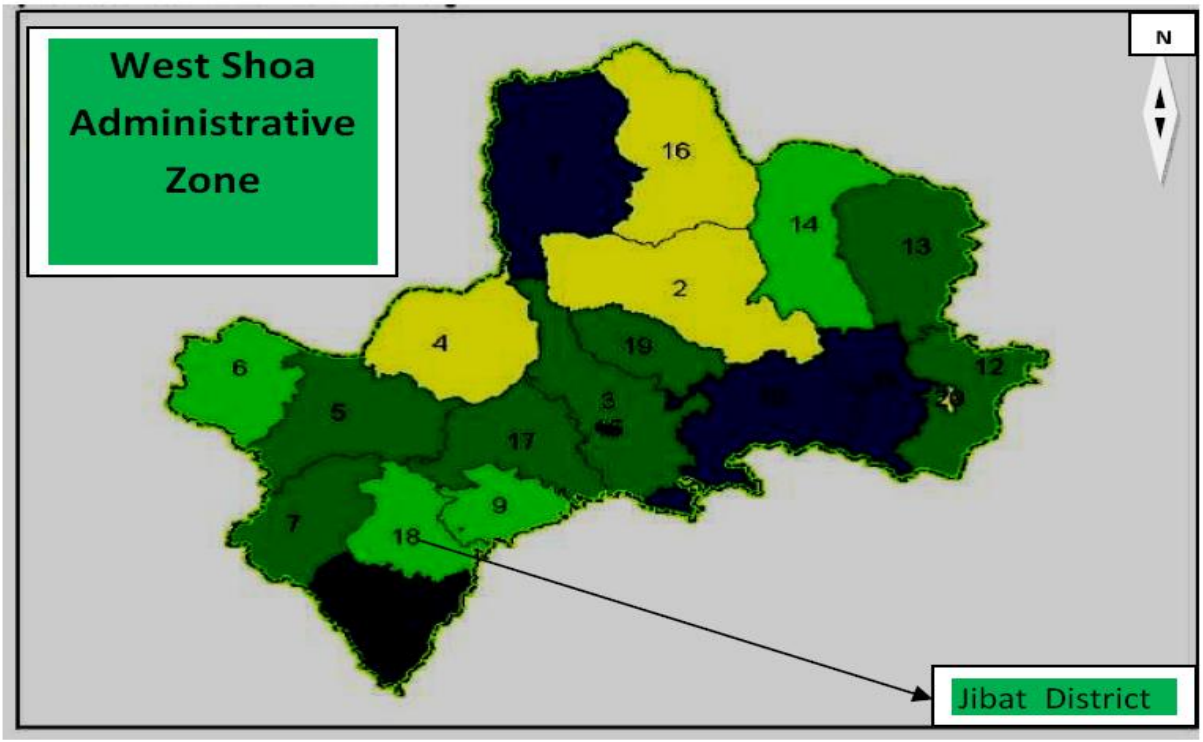
Source: Jibat woreda finance and economic development office, 2012.

Figure 3.2. Location of West Shoa Zone in Oromia Region



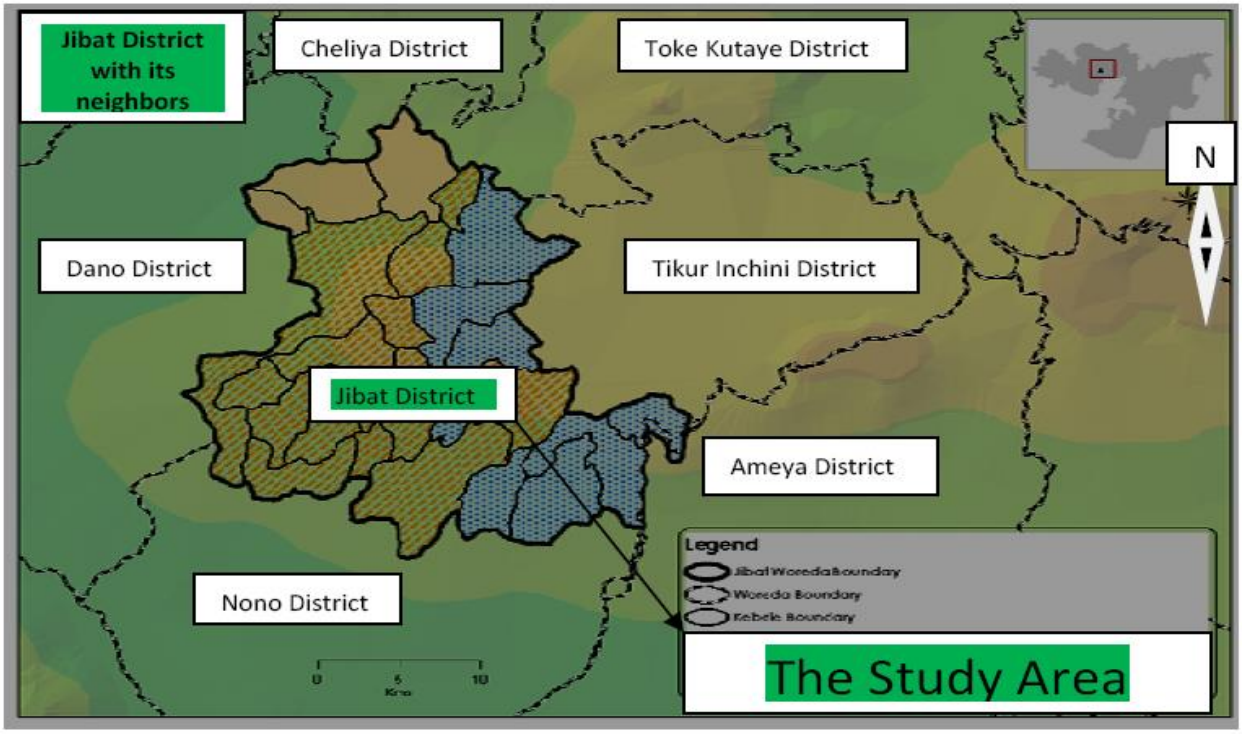
Source: Jibat woreda finance and economic development office, 2012.

Figure 3.3. Location of Jibat District (the study area) in West Shoa Zone



Source: Jibat woreda finance and economic development office, 2012.

Figure 3.4. Location of Jibat District (the study area) with its neighbors



Source: Jibat woreda finance and economic development office, 2012.

3.2 Apparatus and Glasswares

Polyethylene bottles, 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, and POLAND), electronic analytical balance with ±0.00001g precision (AA-200DS, Denver Instrument Company), Micropipette (0–50 µL) , Volumetric flasks (50, 100, 250, 500 and 1000 mL), a 0.45-µm type membrane filter paper (Whatman®, No. 41, England), Funnels, 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® Hot ware, PC 200/210/220), Electric Blast Drier (101-0, Tianjin Taisite Instrument Co. Ltd), a mortar with pestle, a 0.5mm sieve, Conductivity/TDS/Salinity/Resistivity Meter (SCHOTT-GERATE GmbH. Hattenbergstr.10, SX713, TDS working range: 0-100 g/L)), Electrical Thermostatic Water Baths (DK 2000 IIIL, ELICO-SL 194 Double Beam Atomic Absorption Spectrophotometer equipped with deuterium arc back ground corrector and hollow cathode lamps with air/acetylene flame atomizer was used for the analysis of the analyte metals (Cr, Cd and Pd) in the water samples. ELICO-CL 378 Flame photometer was used for K and Na determination and ELICO-SL 160 Double Beam UV-Vis Spectrophotometer were used.

3.3 Chemicals and Reagents

All the chemicals and reagents for the study were of analytical grade. 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. 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™, India) were used for the preparation of 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%, UNICHEM® 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) was used for determination of total alkalinity. $AgNO_3$ (99%, LOBA CHEMIE PVT.LTD.INDIA) was used for argentometric titration for the determination of chloride. $BaCl_2$ (UNI-CHEM® Chemical reagents, India) was used for determination of SO_4^{2-}. Distilled water was used for all preparations and dilutions of solutions.

3.4 Sampling Procedures

3.4.1 Cleaning of Sampling Equipment

All the glassware and materials used during sample collection and experimental work were cleaned before and after use with tap water and detergent, rinsed with distilled water, soaked with 10% (v/v) nitric acid solution, re-rinsed with distilled water and subjected to total air dry to ensure decontamination (free from contamination).The containers were rinsed with sample water prior to actual sample collection before being used for sampling (APHA, 1999).

3.4.2 Water Sampling, Preservation and Transportation

Sampling is obtaining a portion representative of the whole population, the total quantity from which a sample is obtained. Sampling technique helps to ensure that sample quality measurements are accurate and precise estimate of the quality of the population (S.Mitra, 2003).

Samples for chemical and physical parameters were taken from the source water (spring and deep well water). There are many known water springs in the studied rural area and one recently in 2005 E.C established deep well water with 132m depth known as 'Laga Daadaa'. Among these, three water samples (two spring waters and one deep well water) were collected from three different places (laga sose, Laga Abbaa Moggaa, and Laga Daadaa respectively) of Jibat Shenen district and selected for analysis of physicochemical, common cations and anions and some toxic heavy metal parameters. The water samples were collected by following standard sample collection protocol and guidelines given in American Public Health Association (APHA, 1999). Special precautions were taken during the collection of samples. Polyethylene bottles were used in sample analyses because glass bottles absorb metals and therefore will cause inaccuracy to analysis (Roger, 2002). Water samples were treated in three bottles with azide modification methods at each spring sites and deep well water site to fix DO for analysis at the site of sample collection. The collected samples were stored in an ice-box, preserved for the determination of other physico-chemical parameters at a temperature of $4^{o}C$ and transported to the laboratory for analysis (APHA, 1999) for replicate measurements. The water was filtered through a 0.45µm membrane filter as soon as possible after collection. The first 50 - 100 mL of sample was used to rinse the apparatus.

3.5 In situ Analysis for Physical Indicators

3.5.1 Temperature

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

3.5.2 pH

pH was measured with a portable pH-meter. The pH-meter was calibrated with a buffer solution of pH 4.01, pH 7.0 and pH 9.2 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 to each site of water samples.

3.5.3 Electrical Conductivity (EC)

The measurement of conductivity was made *in-situ* or in the field immediately after water sample has been obtained, because conductivity changes with storage time. Thus, EC was measured with a portable conductivity meter.

3.6 Laboratory Sample Analysis

3.6.1 Classical Methods of Analysis

- **TDS**: TDS is the concentration of the dissolved chemicals in sample of water. It was measured using electrical Conductivity/TDS Meter as soon as the samples were transported to the laboratory.
  Procedure: Electrical Conductivity Meter was calibrated by washing with distilled water and then dipped in to the water and measure how well the water conducts electricity. Then, it converts to the concentration of total dissolved solids.
- **DO** determined using azide modification of Winkler method**.** Oxygen present in the sample oxidizes the divalent manganese to its higher valency, which precipitates as brown hydrated oxides after addition of NaOH and KI. Upon acidification, manganese reverts to divalent state and liberates iodine from KI equivalent to DO content in the sample. The liberated iodine is titrated against $Na_2S_2SO_7$ (N/80) using starch as an indicator (Maiti, 2004). Nitrite (NO_2) interference is overcome by the use of sodium azide (NaN_3).

Procedure: 50 mL of sample water was taken with a 250 mL conical flask and closed with stopper. Then the stopper was removed and 1mL of MnSO4 followed by 1mL alkali-iodide- azide reagent was added. Stopper carefully to exclude air bubbles and mix by inverting the bottle a few times. Allow the

brown manganese hydroxide floc (white floc indicates absence of DO) to settle to half the bottle volume, 1 mL of conc. H_2SO_4 was added and re-stopper. Mix by inverting several times until dissolution completed and titrated with standard $Na_2S_2O_3$. Then, DO was calculated using equation 2.1.

- **Alkalinity** in natural water defined as the quantity of base (mainly, OH^-, CO_3^{2-} and HCO_3^-) that react with strong acid when the pH of the sample is lowered to 4.5. In other expression, it is mole of H^{+1} needed to lower the pH of 1 L to 4.5 (Maiti, 2004).

Procedure: 50 mL of sample was taken in a 250 mL conical flask and 2 drops of phenolphthalien indicator was added and titrated with 0.01 N HCl until the color changes from blue to yellow. Then, mL of titrant used to the end point was recorded and the alkalinity of the water sample was calculated using equation 2.3

- **Total Hardness** is expressed as mg/L $CaCO_3$. Common titration methods called Ethylenediaminetetraacetic acid (EDTA).In alkaline condition EDTA or its sodium salt (Na_2EDTA) readily react with calcium, magnesium, and certain other metal cations to form soluble chelated complex.Ca^{2+} and Mg^{2+} ions develop wine red color when small amount of dye such as Eriochrome-Black T (EBT) is added under alkaline condition. When EDTA is added as titrant, Ca and Mg will cqaoplexed with EDTA resulting in sharp change from wine red to blue, which indicates end-point of titration.

$$M^{+2} + EBT \rightarrow \text{(M-EBT) complex}$$

Wine red

$$M^{+2} + EDTA \rightarrow \text{[M-EDTA] complex}$$

Sky blue

Procedure: 50 mL of the sample water was taken in to a 250 mL conical flask and 2 mL buffer solution was added till the pH -10. Then, 2 drops of EBT was added and titrated with standard 0.01M EDTA (with continuous string) until the reddish color disappears and turns to blue. The blank sample (50mL distilled water +2 drops of EBT) was titrated with 0.01M EDTA and hardness is calculated using equation 2.4.

Ca and Mg hardness: 50mL of water sample was taken in 250 titration flask and 2mL of 1N NaOH solution was added to make $_PH$ of 12 to 13. Immediately after addition of the alkali, 2 drops of phenolphthalein indicator was added. Then, the solution was titrated against standard 0.01M EDTA solution. Then, Ca-hardness was calculated using equation 2.5 and Mg-hardness using equation 2.6.

- **Chloride:** A measurement of chloride is necessary to determine the suitable of water for domestic, industrial and agricultural uses. It is measured by titrating a known volume of sample with standardized silver nitrate solution using potassium chromate solution in water (APHA, 1999).

  Procedure: 50 mL of sample water was taken to 250 mL conical flask. 1mL of 0.01M CrO_4^{2-} was added as an indicator and mix thoroughly. The mixture was titrated with standard Ag^{+1} (0.1 N) until yellow color of the solution changed to brick red precipitation (A). The blank titration (B) also done until the color nearly similar to the previous titration i.e. 50 mL distilled water +1 mL of 0.01 M CrO_4^{2-} indicator. Then, the concentration of Cl^- in the studied water was calculated using equation 2.7.

3.6.2 Instrumental Methods of Analysis

FAAS (for heavy metal analysis), flame photometer (for Na and K analysis), and UV-Vis spectrophotometers (for PO_4^{3-} and NO_3^- analysis) were used.

- **General procedure for metal Analysis in water**.

50 mL of water sample was taken in digestion apparatus and 10 mL of conc. HNO_3 was added and digested using hot plate (Kaldjial digestion apparatus) and evaporated to half its volume. The mixture was cooled and filtered using watchman filter paper. The filtrated sample was transferred to 50 mL volumetric flask and diluted to the mark with distilled water. The standards were prepared for the analyte for calibration of AAS and flame photometry. Then the samples were analyzed for the contents using flame photometry (Na and K) and FAAS for other metals.

- **For determination of sulphate**: It is possible to determine the sulphate content of water by using Uv-Visible spectrometry after converting it to colorful compounds.

Procedure: A conditioning reagent was prepared by mixing a 50 mL of glycerol with a solution containing 30 mL concentrated HCl, 30 mL of distilled water, 100 mL 95% ethanol and 7.5 g NaCl. Then, 10 mL conditioning reagent was added to 25 mL of water sample followed by addition of 0.3g $BaCl_2$. The mixture was diluted to 100 mL with distilled water stand for 45 minutes. The standard was prepared using distilled water and the absorbance of both standards and sample was determined against $BaCl_2$ free blank. The analysis was done at a wavelength of 420 nm using ELICO-SL 160 double beam UV-VIS Spectrophotometer and the concentration of sulphate in the water sample was calculated using equation 2.8.

- **For Phosphate Analysis**, 10 mL of each of the standards, blank and samples were measured into a test tube. 1 drop of phenolphthalein indicator was added to the solutions upon which pink colour develops and 5 N sulfuric acid was added drop wise to discharge the color formed. 8mL of combined reagent (50 mL of 5N H_2SO_4, 5 mL of potassium antimonyl tartrate, 15 mL of ammonium molbidate solution, 30 mL of 0.1M of ascorbic acid solution) was added and mix thoroughly. Standard solutions were prepared. After waiting 15 minutes the absorbance of standards and the sample was measured at 690 nm using reagent blank as the reference solution.
- **For nitrate Analysis:** Nitrate is determined by measuring the absorbance at 220 nm in sample containing 1 mL of hydrochloric acid (1 N) in 100 mL sample. The concentration is calculated from graph from standard nitrate solution in range 1-11mg/L as N.

Procedure: Aliquots of Stock nitrate solution (100µg/mL NO_3-N) containing 0.2-8.0 µg/mL of nitrite were transferred in to series of 10 mL calibrated flask. To each flask, 1 mL of 2 mol/L hydrochloric acid solution was added and the solution was shaken thoroughly for 5 min to allow the diazotization reaction to go to completion. Then, 2 mL of 2 mol/L sodium hydroxide solution were added to form an azo-dye and the contents were diluted to 10 mL using water. After dilution to 10 mL with water, absorbance of the red colored dye was measured at 220 nm against the corresponding reagent blank and the calibration graph was constructed.

3.6.2.1 Instruments Working Conditions

Table 4: Instruments operating conditions for calibration and sample analysis

FAAS Working Conditions				
Element	Wavelength (nm)	Slit Width (nm)	Lamp Current (mA)	Oxidant/Fuel
Cr	357.9	2.000	10.6	Air/Acetylene
Cd	326.1	2.500	8.0	Air/Acetylene
Pd	217.0	0.10	5.0	Air/Acetylene
UV-Vis Spectrophotometric Working Conditions				
Parameter	Wave length(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}	

NB: FAAS measurements for all metals were made using an air-acetylene

3.6.2.2 Preparation of Stock Solutions.

Stock solutions were prepared by weighing out a specific amount of metal (salt) and the metal was transferred into a 100 mL volumetric flask. The metals were dissolved completely by adding deionized water (Greenberg, Clesceri & Eaton, 1992).

Metal stock standards

Stock standard solutions of each of the metals of interest were prepared from high purity metals and reagent grade salts using distilled water, nitric acid and hydrochloric acid based on the individual analysis sheets for specific instruction of the instruments. The stock solutions were prepared at concentrations of 1000 mg/L of the metal.

For Cd and Cr commercially available 1000 mg/L solutions were used. For Na and K 1000 mg/L solution was prepared by dissolving 3.7348 g K_2CrO_4, 2.5418g NaCl dried at 140 ^oC and 1.907g KCl dried at 110 ^oC in distilled water respectively and diluting to 1 L.

Stock lead solution was prepared by dissolving 0.1599 g lead nitrate, Pb $(NO_3)_2$ (minimum purity 99.5%), in approximately 200 mL water by adding 10 mL conc. HNO_3 and dilute to 1000 mL with water. A commercial standard solution of 1000 g mL^{-1} of lead for atomic absorption spectrometry (BDH Ltd) was used as the stock standard solution. Working standard solutions were diluted from the stock standard solution with a 0.1 M nitric acid solution.

Reagents Preparation for Phosphate and Nitrate Analysis

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

3.6.2.3 Working Standard Solutions

Working solutions are the solutions prepared from the stock solution through dilution in the appropriate solvent at the concentration requested for spiking the matrix. In this study, working standard solutions of each metal were prepared freshly by diluting the intermediate standard solutions (100 mg/L, each) by taking 10 mL of individual metal stock solutions in a separate 100 mL volumetric flasks and diluting to the mark with distilled water.

3.6.2.4 Calibration of metal Standard Solutions

The calibration standard solutions were used to calibrate the instrument response with respect to the analyte concentration. A blank and five calibration standard solutions of different concentration levels were prepared for each metal from the respective working standard solutions (100 mg/L). These calibration standard concentrations were within the working linear range of the instrument used for analysis. Beginning with the blank and working toward the highest standard, the solutions were aspirated and the readings were recorded. The prepared calibration standards: 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 each analytes are given in Table.

Table 5: Prepared calibration standards for Cd, Cr, Pb, Na, K, NO_3^- and PO_4^{3-}.

Analyte	Calibration Standard Solutions (mg/L)					
	S_0	S_1	S_2	S_3	S_4	S_5
Cd	0.0	0.25	0.5	0.75	1.0	1.25
Cr	0.0	1.5	2.5	3.5	4.5	5.5
Pb	0.0	0.5	1.0	2.0	4.0	8.0
Na	0.0	0.5	1.5	2.5	3.5	4.5
K	0.0	0.5	1.5	2.5	3.5	4.5
NO_3^-	0.0	0.5	1.0	3.0	5.0	7.0
PO_4^{3--}	0.0	0.40	0.80	1.20	1.60	2.00
SO_4^{2-}	0.0	15.00	20.00	25.00	30.00	35.00

3.6.2.5 Spiking Metal Standard Mixture solution

Spiking is done by adding a known quantity of a component that is similar to the analyte but not present in the sample originally. Its practical approach is to spike the concentration to reach near the midrange calibration point (Zhang, 2007). Standard mixture solution containing all the metals of interest at varying concentrations (Cd = 25, Cr = 125, Pd=100, Na = 125 and K = 31 mg/L) was prepared by taking 2.5, 12.5,10, 12.5 and 3.1 of Cd, Cr, Pd, Na, and K stock standard solutions (1000 mg/L), respectively, in to 100 mL volumetric flask and diluting to volume with distilled water.

3.6.2.6 Water Digestion Procedure

In this study, a wet acid-digestion method using the mixture of HNO_3 was used for preparation of water samples. Five replicates of 100 mL water samples (filtered through Whatman No. 41 filter paper) were taken into 150 mL Erlenmeyer flasks for each springs and acidified with 5 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 were now ready for FAAS analysis (Maiti, 2004).

3.6.2.7 Estimation of Detection Limits

Instrument Detection Limit (IDL)

The IDL is the concentration of the analyte that produces a signal greater than five times the signal-to-noise ratio of the instrument. Instrument detection limit for each metal was determined from analyses of seven replicates of analyte free water (Table 10) and seven replicate measurements of their respective calibration blanks at their specific wavelengths (USEPA, 2007) and recording instrument signals. The IDL were calculated by using the following equation,

$$IDL = SD \times 3 \quad \text{.....(3.1)}$$

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

Method Detection Limit (MDL)

A method's **detection limit** is the smallest amount or concentration of analyte that can be detected with statistical confidence different from a blank (99% confidence) (David Harvey, 1956). It is obtained by the mean reagent blank signal (X_{blank}) plus three times the standard deviations of the mean reagent blank signal (S_{blank}) (Ebdon *et al.*, 1998; Mitra, 2003; Miller and Miller, 2010).

$$\text{i.e. } LOD = X_{blank} + 3S_{blank}\text{ , n = 7} \quad \text{..... (3.2)}$$

In the present study, method detection limit for each metal was estimated for water samples analysis, from seven replicate measurements of reagent water spiked with the target analyte at a concentration four times the IDL. 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. 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 analytes.

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.

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……..…….…….…... (3.3)

Where SD s 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).

Limit of Quantification

The lowest concentration level at which a measurement is quantitatively meaningful is called the limit of quantitation (LOQ) (Mitra, 2003). The LOQ was calculated by multiplying standard deviation of the reagent blank by ten plus the mean of the reagent blank signals (Miller and Miller, 2010) and the results were indicated in Table 10.

LOQ = X_{blank} + 10 x S_{blank} , n = 7 …… (3.4)

3.6.5 Evaluation of Analytical Precision, Accuracy and Recovery

Accuracy of the analytical methods was evaluated in terms of %recoveries from a sample matrix. The analytical method precision was assessed in terms of relative percent differences (RPD), relative standard deviation (RSD) and standard deviations (SD) among measurements. To determine a spike recovery (the recovery of a known spiked analyte)**,** the blank or sample is split into two portions, and a known amount of a standard solution of the analyte is added to one portion. The concentration of the analyte is determined as,

$$\%R = \frac{F-I}{A} \quad \text{……..3.5}$$

Where, %*R*= the percent recovery, F= Spiked portion, I= unspiked portions and *A* is the concentration of the analyte added to the spiked portion.

If the recovery for a field spike is unacceptable, then a sample is spiked in the laboratory and analyzed immediately. If the recovery for the laboratory spike is acceptable, then the poor recovery for the field spike may be due to the sample’s deterioration during storage (David Harvey, 1956).

4. RESULTS AND DISCUSSION

4.1 Physico-chemical Parameters of Water Samples

The mean values of Physico-chemical Parameters of Water Samples were obtained from three replicate measurements. The results (mean ±SD) are given in Table 5.

Temperature: The measurements were made to observe the variation in water temperature at each site. Thus, the variation of the temperatures investigated at site of Laga Sose, Laga Abba Mogga and Laga Dada were 21.7^{o}C, 20.8^{o}C, and 23.27^{o}C respectively. Then, the observed variation for temperature on each site is below the WHO (Appendix I). The reported results (Table 5**)** are the average of the three measurements that were taken as the average of three replicates at each springs and deep well source.

pH: pH has no direct adverse effect on human health, however, according to WHO guidelines, the maximum desirable limit of pH is 7.0-8.5 and USEPA established pH limits from 6.5-8.5. The pH at site of Laga Sose, Laga Abba Mogga and Laga Dada were 5.7, 6.54 and 8.2 respectively. Waters with pH lower than 4 have a sour taste and above 8.5 are an alkaline bitter taste. pH below 6.5 starts corrosion in pipes, thereby releasing toxic metals such as Zn, Pb, Cd, Cu, etc. The pH values of the studied spring and deep well waters were compared with the guideline values for water quality (Appendix I). Out of the three samples analyzed, the laga dada deep well had pH value between 8.2 which characterized basicity, but all the samples analyzed had pH within the prescribed limits recommended by USEPA guideline.

Table 6: Mean* ± SD values for physico-chemical parameters of spring waters

Parameter	Water Sites		
	Laga Sose Mean ± SD	Abba Mogga Mean ± SD	Laga Dada Mean ± SD
Temperature (^{o}C)	21.7 ± 0.35	20.85 ± 0.52	23.27±0.42
pH	6.67 ± 0.1 4	6.76 ± 0.20	8.2 ± 0.06
EC (µS/cm)	47.10 ± 2.46	46.40 ± 1 .35	27.80 ± 0.94
TDS (mg/L)	32.90 ± 0.50	31.60 ± 0.55	18.00 ± 0.71
TA (as mg $CaCO_3$/L)	5.76 ± 0.80	6.12 ± 0.40	7.20 ± 0.64
TH (as mg $CaCO_3$/L)	27.60 ± 0.91	25.20 ± 1.79	18.80 ± 1.1 0
DO (mg/L)	9.140 ±1.232	22.043 ± 2.030	17.204 ± 1.232

* Mean values are calculated from three replicates.

Electrical Conductivity (EC): Conductivity is the capacity of water to carry an electrical current and varies both with number and types of ions in the solution, which in turn is related to the concentration of ionized substances in the water (Maiti, 2004). Most dissolved inorganic substances in water are in the ionised form and hence contribute to conductance. It is a valuable measure of the amount of cations and anions in water. In this study, mean values determined were 47.10 ± 2.46 (Laga sose), 46.40 ± 1 .35 (laga Abba Mogga) and 27.80 ± 0.94 (Laga Dada) respectively.

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; drinking-water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/L. The measured TDS mean values of the water sample studied were 32.90 ± 0.50 (Laga Sose), 31.60 ± 0.55 (Abba Mogga) and 18.00 ± 0.71 (Laga Dada). The TDS values from each springs and deep well waters are below the WHO and different national guidelines for drinking water quality (Appendix I).

Dissolved oxygen (DO): In the present study, the mean value for DO in Laga Sose spring, laga Abba Mogga spring and Laga Dada deep well were 9.140 ±1.232 mg/L, 22.043 ± 2.030 mg/L and 17.204 ± 1.232 mg/L respectively (Table 5).

Total Alkalinity (TA): The TA was calculated using eqn. (2.3). All water having pH< 8.5 contain basicity. Thus, when total alkalinity was estimated, titration with phenolphthalein colorless which characterize basic and titration with methyl orange is pink colour because methyl orange has pH<4 which indicates acids. 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 which indicates complete neutralization of OH^- and CO_3^{2-}. The major portion of alkalinity in natural waters is caused by hydroxide, carbonate and bicarbonate. Therefore, the observed alkalinity is possibly due to HCO_3^- from dissolved CO_2. The mean value of the present study result of TA was found 27.60 ± 0.91 (Laga Sose), 25.20 ± 1.79 (Laga Abba Mogga) and 18.80± 1.10 (Laga Dada) as shown in Table 5. The results indicate that Laga Dada deep well 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 and deep well 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.

Total Hardness (TH): The TH was determined by EDTA titration method and calculated by using equation (2.4). The TH mean value of the present study showed that water hardness is high in Laga Sose spring water (27.60 ± 0.91mg/L) and low in Laga Dada deep well water (18.80 ± 1.1 0 mg/L) as

shown in (Table 5), 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.

4.2 Major Chemical Parameters of Water Samples by Classical Methods

Calcium (Ca) and Magnesium (Mg):

Calcium and magnesium ions dissolved in water are the two most common minerals that make water "hard." The degree of hardness becomes greater as the calcium and magnesium content increases. The concentration of dissolved magnesium ion is lesser than the concentration of suspended magnesium. **Calcium (Ca)** is determined by EDTA titration method and calculated in mg/L by using the formula given in equation 2.5. In the studied sample water, the highest concentration of calcium (7.37mg/L) was detected in Laga Sose and the lowest (5.13 mg/L) in Laga Dada deep well sample (Table 7). The concentrations of all samples are within EPA standard limit which temporary hardness is caused by a combination of calcium ions and bicarbonate ions in the water.

Mg is calculated from the Ca concentration and TH, using the formula given in equation 2.6. In the studied sample the highest concentration of magnesium (2.23mg/L) was detected in Laga Sose sample and the lowest (1.45 mg/L) in Laga Dada sample. The amounts of magnesium detected in all three samples fall within the EPA standard limit (Appendix I).

The Ca and Mg of the investigated spring and deep well waters could be due to the contact between the water body and the rock layers. Because these springs and deep well are naturally occurred springs and deep well that come out on the earth's surface by crossing rock layers which leach these minerals and others to the water body. All the three samples were categorized under soft water. Soft water is more likely to dissolve certain metals such as cadmium and lead, which are potentially toxic from pipes than hard water. Hard water is not a health hazard. The study results for Ca and Mg are below the current recommended maximum value for drinking water (Appendix I). The results are given in Table 5.

Sulphate (SO_4^{2-}): 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). This indicates, on comparison with other guideline values for drinking water, no problem associated with SO_4^{2-} of the studied waters. The SO_4^{2-} in the studied spring and deep well waters might be due to atmospheric deposition of particulate matter

and natural sources in the waters. The SO_4^{2-} in the studied water springs and deep well were undetected because its concentration at the absorbance of 420 nm is almost zero (Table 7) and are graphically shown in Figure 3.

Chloride (Cl^-): Chloride in drinking-water originates from natural sources, sewage and industrial effluents (WHO, 2011). The Cl^- concentration in the investigated water springs and deep well were 4.10 mg/L for Laga Sose, 4.00 mg/L for Laga Abba Mogga and 3.10 mg/L in Laga Dada. Chloride may affect acceptability of drinking water by offering a salty taste to water. As reported in Table 6, the Cl^- values determined for all spring and deep well sources are below the current guideline values for drinking, indicating that no taste effects associated with the studied springs and deep well (Table 7). Therefore, the Cl^- ions in the studied springs and deep well 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, not of health concern at levels found in drinking-water (WHO, 2011).

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).

In this study, the mean values obtained were ranged from the minimum value of 5.567 to 21.833mg/L for Na and from 0.333 to 7.067 mg/L for K (Table 7). 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 and no health risks concerned with K at levels found in this water.

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).

Nitrate (NO_3^-): Nitrate is an important plant nutrient and causes eutrophication in receiving water bodies. High concentration in drinking water (>40 mg/L) may cause blue-baby disease (Maiti, 2004). The NO_3^- in the studied waters was might resulted due to the natural availability of NO_3^- in water. The

average concentrations of NO_3^- (Table 7) in the studied waters were 9.548 mg/L (Laga Sose), 4.643 mg/L (Abba Mogga) and 1.975 mg/L (Laga Dada).The highest concentration value for laga sose spring water might be resulted from the waste products in human and animal excreta that might also contribute to NO_3^-. However, 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.

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. Groundwater, therefore, is more likely to have higher PO_4^{3-}concentration (Maiti, 2004). The PO_4^{3-} in the studied springs and deep well waters was possibly from the natural contact with minerals when the water bodies come across the layers of various minerals. The obtained results were 0.010 mg/L in Laga Sose spring water, 0.015 mg/L in Abba Mogga spring water and 0.009 mg/L in Laga Dada deep well water (Table 7). 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).

4.5 Sample Analysis by Flame Atomic Absorption Spectrometry (FAAS)

The results for analyzed trace metals in water samples are given in Table 7.

Cadmium (Cd): Cadmium can be released to drinking water from the corrosion of some galvanized plumbing and water main water piping materials. Higher levels of cadmium may be found in water near industrial areas or hazardous waste sites. The EPA standard level for cadmium is 0.003 ppm (Soylak, Divrikii, Saracoglu & Elci, 1998). The EPA has discovered that cadmium has high potential to cause health effect like nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock and renal failure in short period of time. In a lifetime exposure to cadmium at levels exceed 0.005 mg/L can cause kidney, liver, bone and blood damage (Ideris, 2008**).**

In this study, Cd concentrations in springs and deep well 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 WHO 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. Furthermore, the waters can be used for drinking purpose since the MDL was below the guideline values for water quality (Appendix I).

Chromium (Cr): The chromium metal gets into drinking water through certain industrial facilities where sodium dichromate solutions (hexavalent) were used to prevent corrosion in piping (Maiti, 2004).. Eventually, chromium VI will be reduced to chromium III by organic matter. Chromium III contamination exit 0.1 mg/L can affect internal hemorrhage, respiratory disorders and kidney damage, while chromium VI can cause dermatitis and ulceration (Ideris, 2008). In the presented study, like Cd, the Cr concentrations in the studied springs and deep well waters were also found to be below the MDL (0.05 mg/L) as indicated in Table 9 because no industry involving chromium in the studied area. 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.

Lead (Pb): Lead concentration in surface and ground raw water range from traces to 0.04 mg/L, averaging about 0.01 mg/L.). In this study, the concentration of Pb in the studied springs and deep well waters were found to be below the maximum permissible value recommended by WHO (0.05 mg/L) as indicated in Table 7.

Table 7: Mean* ± SD (in mg/L) of major chemicals and heavy metals in water samples.

Parameter	Water Sites		
	Laga Sose	Laga Abba Mogga	Laga Dada
Ca	7.37 ± 0.22	7.05 ± 0.36	5.13 ± 0.33
Mg	2.23 ± 0.32	1.84± 0.21	1.45 ± 0.17
Cl^-	4.10 ± 0.42	3.10 ± 0.22	4.00 ± 0.35
SO_4^{2-}	UD	UD	UD
Na	6.533 ± 0.208	5.567 ± 0.115	21.833 ± 0.493
K	7.067 ± 0.208	0.333 ± 0.058	1.967 ±0.153
NO_3^-	9.548 ± 0.754	4.643 ± 0.636	1.975 ± 2.310
PO_4^{3-}	0.010 ± 0.001	0.015 ± 0.001	0.009 ±0.000
Cd	<MDL**	<MDL	<MDL
Cr	<MDL	<MDL	<MDL
Pd	0.5±0.1	0.3±0.05	0.5±0.08

*Measurements were made in three replicates. * * < MDL: Less than Method Detection Limit.

4.6 Calibration curve results

In this study, calibration curves showing absorbance versus concentration at a specified wavelength were prepared for each metal through direct analysis of the instrument blank and five calibration metal standard solutions. For Na and K, the calibration graphs plotted as instrument response versus prepared concentration showed the R^2 values of 0.998 and 0.9987 for Na and K , respectively, which are greater than the minimum acceptance value of 0.995 (APHA, 1999) indicate that no problem concerning the performance of the method. This showed that there was a linear between the instrument response and prepared concentration indicating the best working condition of the instrument. The calibration graphs are given in Appendix II. For NO_3^- and PO_4^{3-} the two calibration curves show good correlation coefficients of 0.9997 and 0.9995, respectively, which are greater than the minimum acceptance value of 0.995 (APHA, 1999) as given in Appendix III. For a total of 3 heavy metals (Cd, Cr and Pb) analyzed, the correlation coefficients (R^2) were 0.9963, 0.9996 and 0.998 respectively 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 curve of Chromium was given in Fig. 4.1 as an example while the rest are in the Appendix IV.

The concentrations of the calibration standards and value of correlation coefficient of the calibration graph for each parameter with which the Flame photometry, Uv-Visible spectroscopy and FAAS calibrated were listed in Table 8. Calibration curves for the various concentration ranges showed good correlation coefficients ranged between 0.9993 and 0.999 (Table 9), which were all greater than the required limit (0.995) for trace element analysis (EPA, 2007). This showed that there was good correlation (or relationship) between concentration and absorbance indicating good calibration of the instrument.

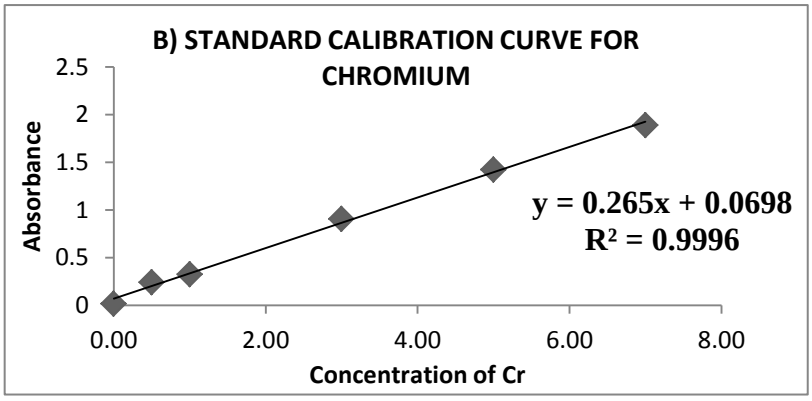


Figure 4.1: Standard calibration curve of chromium

Table 8: Calibration standards and correlation coefficients of the calibration curves for determinations of metals using Flame photometry, Uv-Vis spectroscopy and FAAS.

Metals	Concentration of Calibration standards (mg/L)	Correlation coefficient of calibration curves (R^2)	Calibration equation
Na	0.50,1.50,2.50,3.50,4.50	0.998	y = 1.0017x + 0.0114
K	0.50,1.50,2.50,3.50,4.50	0.9987	y = 0.9825x + 0.048
NO_3^-	0.50, 1.00, 3.00, 5.00, 7.00	0.9969	y = 0.265x + 0.0698
PO_4^{3-}	0.20, 0.40, 0.80, 1.20, 1.60	0.9999	y = 0.4716x + 0.0049
SO_4^{2-}	5.00, 10.00, 15.00, 20.00,25.00	0.9993	y = 0.0107x + 0.0126
Cr	1.50, 2.50, 3.50, 4.50, 5.50	0.9996	y = 0.0132x + 0.0024
Cd	0.250, 0.50, 0.750, 1.0, 1.250	0.9991	y = 0.0825x + 0.0021
Pb	0.50, 1.0, 2.0, 4.0, 8.0	0.998	y = 0.015X+0.005

N.B: Concentrations of calibration for calibration curve are taken from five points.

4.8 Method Precision and Accuracy

i) Method Accuracy

The accuracy solutions are prepared by spiking a known quantity of authentic samples and estimated from the recovery of a known standard spiked into the sample. For evaluating the analytical method accuracy, recovery studies were made on triplicates of each sample fortified at near mid-range calibration concentrations (4.0 mg/L of K and Na, 2.5 mg/L Cr, 3.0 mg/L of Pd and 0.5 mg/L of Cd). As given in Table 9, the mean percent recovery values ranged between the highest 99.583 (K in Laga Sose) and lowest 92.583 (Na in Laga Sose), all lied in the acceptable range (80–120%) for metal analysis (US EPA, 2008). This showed that the analytical method provided results in the required level of accuracy.

ii) Method Precision/ Repeatability/

Repeatability of a method can be determined by multiple replicate preparations of the same sample. In this study, to evaluate whether the digestion procedure and instrumental measurements provide precise data, the Precision/ Repeatability/ was done by preparing three replicates at three different concentrations using sample spikes. For doing so, triplicates of each sample each spiked at near mid-range calibration concentrations (4.0 mg/L of K and Na, 2.5 mg/L Cr, 3.0 mg/L of Pd and 0.5 mg/L of Cd) were digested and analyzed following the same analytical procedure as samples and the percent

RSD and confidence level of these results were reported to illustrate the method repeatability. The RSD values obtained (Table 9) were all under the required limit (≤15%) (Csuros and Csuros, 2002). This indicated that the analytical method, which covers digestion and instrumental measurement steps, has provided acceptable repeatability or precision (Table 9).

Table 9: Recovery and precision test from sample spike (n= 3)

Metal	Sample Code	Conc. in sample (mg/L)	Amount spiked, (mg/L)	Conc. in spiked sample (mg/L)	Accuracy (Recovery, %)	Precision (RSD, %)
K	Laga Sose	129.90±1.572	4.0	133.883±1.815	99.583±6.29	6.318
	Abba Mogga	104.467±0.896	4.0	108.273±0.983	95.167±2.67	2.809
	Laga Dada	24.033±0.839	4.0	27.757±0.905	93.083±2.89	3.1 13
Na	Laga Sose	2.60±0.520	4.0	3.637±0.520	92.583±4.54	4.908
	Abba Mogga	6.033±0.153	4.0	10±0.436	99.167±12.5	12.689
	Laga Dada	6.433±0.208	4.0	10.403±0.443	99.25±7.233	7.287
Cd	Laga Sose	0.022±0.0076	0.5	0.503±0.025	96.267±4.20	4.922
	Abba Mogga	0.0133±0.0049	0.5	0.50±0.0312	97.88±6.125	6.245
	Laga Dada	0.6067±0.0513	0.5	1.088±0.0208	96.333±6.11	1.913
Cr	Laga Sose	1.487±0.0231	2.5	3.956±0.0311	98.79±1.652	0.786
	Abba Mogga	1.065 ±0.117	2.5	3.538 ±0.0544	98.938±2.59	1.537
	Laga Dada	4.187 ±0.326	2.5	6.564 ±0.387	95.097±2.57	5.898
Pb	Laga Sose	8.1±1.153	3.0	10.929±1.1325	94.3±2.917	10.362
	Abba Mogga	77.733±11.01	3.0	80.604±11.002	95.7±2.079	13.649
	Laga Dada	21.583±1.465	3.0	24.469±1.481	96.178±1.87	6.053

RSD*= Relative standard deviation

4.8 Detection Limits Results

- **Instrument Detection Limit (IDL)**

The IDL of each of the analytes were determined from seven replicate measurements of the instrument blanks and calculated using equation (equation 3.1); these are below the respective method detection limits (Table 10), indicating good sensitivity of the measuring instrument for analyses (Csuros and Csuros, 2002; Patnaik, 2010). For NO_3^-, seven replicates of distilled water treated with 0.1 N HCl was analyzed as an instrument blank for IDL determination. For PO_4^{3-}, seven replicates of distilled water

treated with ammonium molybdate and stannous chloride reagent were analyzed as an instrument blank for IDL determination. For Cd, Cr and Pd the IDL was determined through analysis of distilled water as calibration blank. The results are given in Table 10.

- **Method Detection Limits (MDL)**

The MDL of the analytical methods for each analyte were determined from seven replicates of laboratory reagent spiked with the target analyte at a concentration of the method blanks and calculated using equation (3.3). These calculated values (Table 10) 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 10 times of calculated MDL, and also evaluated in terms of recovery and RSD. The recovery and RSD of the calculated MDL are within the required limit: 80-120% for recovery and ≤ 20% for RSD (APHA, 1999). The MDL values lied in the range 0.50 (Cd Laga sose spring) to 3.97 (K in Laga Abba mogga spring) mg/L. These show that the methods are well validated for the determination of the analytes.

- **Method Quantitation Limit (MQL)**

The MQL for each metal analyte were calculated from the instrument response of seven replicates of the method blanks using the respective regression equations of the calibration curves and equations 3.4. MQL values 1.02 (Cd in Laga sose spring) to 7.09 (K in Laga sose spring) mg/L (Table 10). All the values were found to be in or below the required limit given in APHA, 1999. This indicated that the method was well applicable for the determination of the concentration of metals in water.

Table 10: Instrument detection limit, method detection limit and method quantitation limit for metals of interest determined in water samples.

Metals	**IDL** (mg/L)	**MDL**(mg/L)			**MQL**(mg/L)		
		SW1	SW2	DW3	SW1	SW2	DW3
K	0.72	3.97	3.60	3.90	7.09	6.28	6.91
Na	0.40	3.11	2.01	2.66	7.02	3.57	4.50
Cr	0.13	0.73	0.60	0.77	1.89	1.59	1.99
Cd	0.06	0.50	0.51	0.76	1.02	1.05	1.68
Pb	0.59	1.20	2.30	3.36	3.08	3.97	4.59

5. CONCLUSION AND RECOMMENDATIONS

Safe water is a precondition for health and development. “Water quality” is a term used to express the suitability of water to sustain various uses or processes. Any particular use will have certain requirements for the physical, chemical or biological characteristics of water; for example limits on the concentrations of toxic substances for drinking water use, or restrictions on temperature and pH ranges for water supporting invertebrate communities. Consequently, water quality can be defined by a range of variables which limit water use. The quality of water may be described in terms of the concentration and state (dissolved or particulate) of some or all of the organic and inorganic material present in the water, together with certain physical characteristics of the water.

In this study, two densely populated spring waters (Laga Sose and Laga Abba Moga) and one recently established deep well (Laga Dada) of Shenen Jibat rural area, Weast Shoa, were analyzed for physico-chemical parameters (temperature, pH, EC, TDS, DO, TA, and TH); for common cations and anions (Ca, Mg, Na, and K and SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-) respectively and some toxic heavy metals (Cd, Cr and Pb). During the study temperature, pH and EC were measured at site of sample collection. The TA, TH, SO_4^{2-}, Cl^- , Ca and Mg were determined by classical methods of analysis in laboratory. PO_4^{3-}, NO_3^-, TDS, Na, K and heavy metals were determined by instrumental methods of analysis in laboratory. All the analysis was carried out according to the procedures given in the standard methods (APHA, 1999). The obtained results of all the parameters were compared between the water springs and deep well water with different recommended international guidelines value. Among the three heavy metals Cd and Cr in water samples were below the MDL and SO_4^{2-} was not detected at wavelength 420 nm. The current study results were compared with WHO and different national guidelines for drinking water quality such as USEPA and ES, and all analyzed parameters 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. Therefore, this study recommended that further studies need to be done on heavy metals like F^-, As, Ni, etc, and the biological quality of the waters in order to improve the acceptability of the waters for drinking. Since studies has been done on the area it is also suggested that the new investigation and recommendation of parameters should be done on the other water springs in Shenen Jibat area in order to evaluate whether or not having any health risks concerned (Alberta Agriculture 2002).

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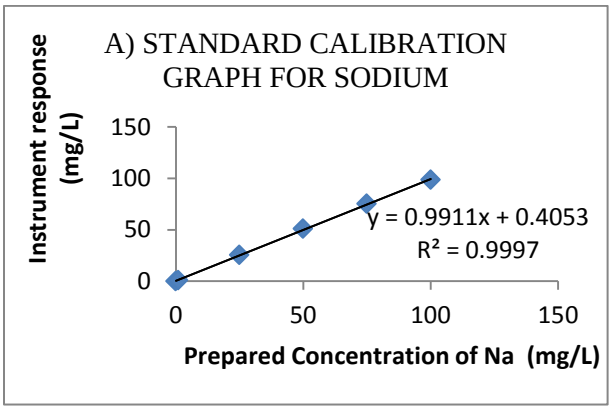
7. APPENDICES

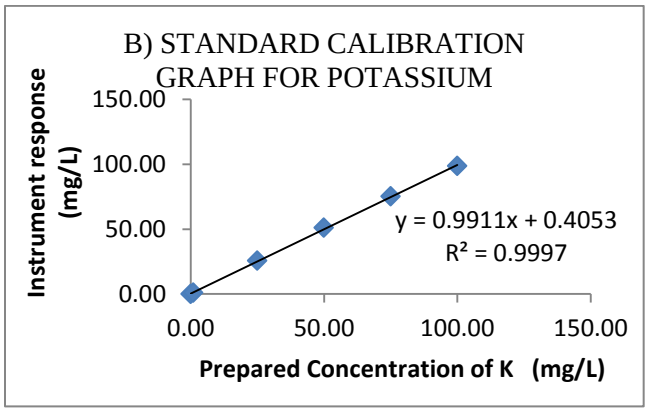
Appendix I: Comparison of the statistical analysis of current results of spring and deep well water in the studied area with different national and international organizations.

S. NO	Parameters	Mean value of Water site			Guidelines for Drinking Water Quality (for *health risk and aesthetic value*)		
		Laga Sose spring	Laga Abba Mogga spring	Laga Dada deep well	ES (2011)	USEPA (2012)	WHO (2011)
1	Temp.(^{0}C)	20.85 ± 0.52	1 9.78 ± 0.42	21.07 ± 0.35	NM[a]	<25	<25
2	EC(µS/cm)	47.10 ± 2.46	46.40 ± 1 .35	27.80 ± 0.94	NM	NM	-
3	pH (mg/L)	6.67 ± 0.1 4	6.76 ± 0.20	8.2 ± 0.15	6.5- 8.5	6.5 - 8.5	6.5 - 8.2
4	TDS(mg/)	32.90 ± 0.50	31.60 ± 0.55	18.00 ± 0.71	1000	500	<600
5	DO (mg/L)	9.140± 1.232	2.043 ± 2.030	17.20 ± 1.232	-	-	-
6	TA (mg/L)	5.76 ± 0.80	6.12 ± 0.40	7.20 ± 0.64	200	NM	NM
7	TH (mg/L)	27.60 ± 0.91	25.20 ± 1.79	18.80 ± 1.1 0	300	NM	200
8	Na^+ (mg/L)	6.533 ±0.208	5.567 ± 0.115	21.833± 0.493	200	< 20	200[b]
9	K^+ (mg/L)	7.067± 0.208	0.333 ± 0.058	1.967 ± 0.153	1.5	NM	NM
10	Mg^{+2}(mg/L)	2.23 ± 0.32	1 .84 ± 0.21	1.45 ± 0.17	50	NM	NM
11	Ca^{+2} (mg/L)	7.37 ± 0.22	7.05 ± 0.36	5.13 ± 0.33	75	75-100	75
12	Cl^- (mg/L)	4.10 ± 0.42	3.10 ± 0.22	4.00 ± 0.35	250	250	250[b]
13	SO_4^2 (mg/L)	UD	UD	UD	250	250[b]	250[b]
14	PO_4^2(mg/L)	0.010± 0.001	0.015 ± 0.001	0.009 ± 0.000	NM	NM	NM
15	NO_3^-(mg/L)	9.548 ±0.754	4.643 ± 0.636	1.975 ± 2.310	50	50	50
16	Cr(mg/L)	<MDL	<MDL	<MDL	0.05	0.1	0.05
17	Cd (mg/L)	<MDL	<MDL	<MDL	0.003	0.005	0.003
18	Pb (mg/L)	0.01	0.14	0.04	0.02	0.05	0.05

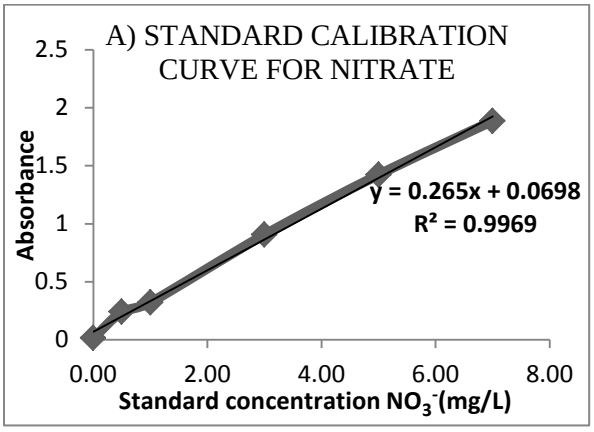
[a] NM: Not Mentioned [b] Aesthetic Based Value

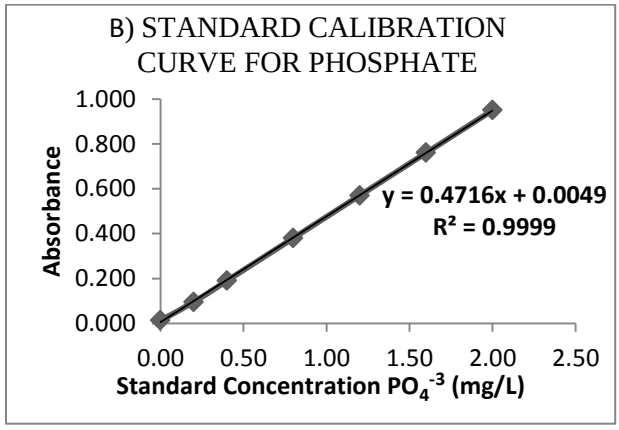
Appendix II: **Flame photometric standard calibration graph for Na and K**





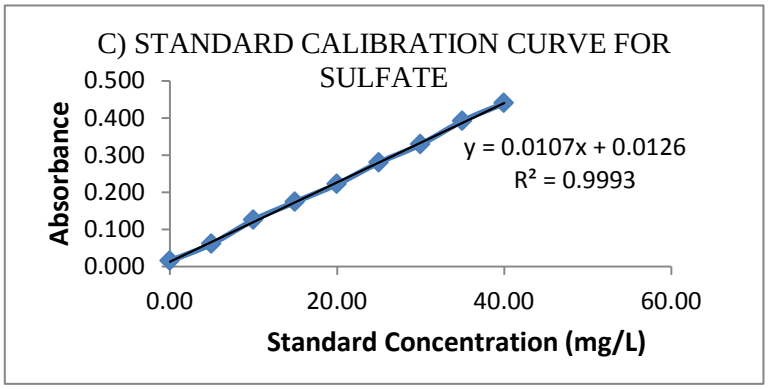
Appendix III: UV-Vis Spectrophotometric standard calibration curve for NO_3^- , PO_4^{3-} and SO_4^{2-}.





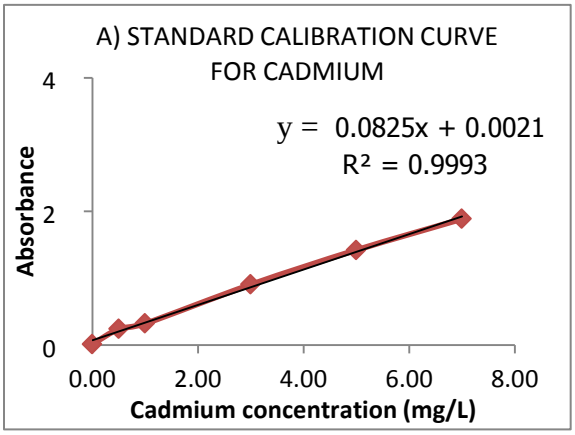
A) Ccalibration curve for NO_3^-

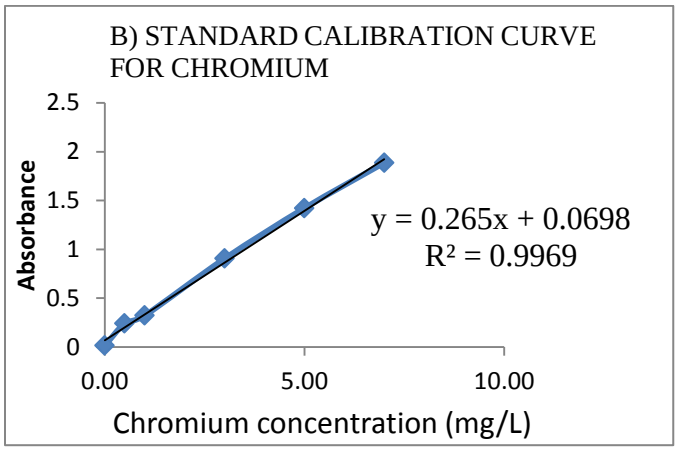
B) Calibration curve for PO_4^{3-}



C) Calibration curve for SO_4^{2-}

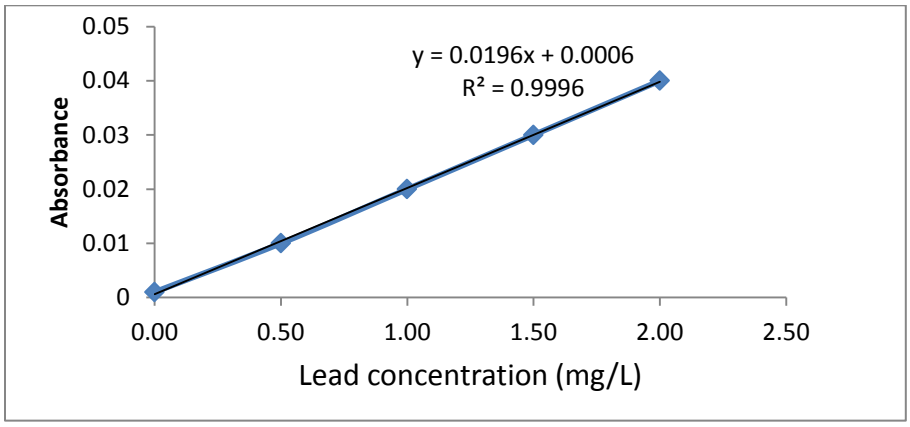
Appendix IV: AAS Spectroscopy standard calibration curve for Cd, Cr and Pb





A) Calibration curve for Cd.

B) Calibration curve for Cr



B) Calibration curve for Pb