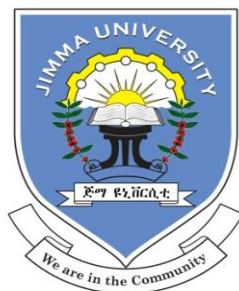


**JIMMA UNIVERSITY  
SCHOOL OF GRADUATE STUDIES  
COLLEGE OF NATURAL SCIENCES  
DEPARTMENT OF CHEMISTRY**



**M.Sc THESIS ON  
PHYSICO-CHEMICAL ANALYSIS AND DETERMINATION OF THE  
LEVEL OF SOME SELECTED HEAVY METALS IN PROTECTED  
SPRING WATER OF JIMMA TOWN**

**October, 2015  
Jimma, Ethiopia**

**M.Sc THESIS SUBMITTED TO SCHOOL OF GRADUATE STUDIES,  
DEPARTMENT OF CHEMISTRY, JIMMA UNIVERSITY IN PARTIAL  
FULFILLMENT OF THE REQUIREMENTS FOR DEGREE OF MASTERS  
OF SCIENCE (M.Sc) IN CHEMISTRY (ANALYTICAL)**

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## **LIST OF ABBREVIATIONS**

AAS- Atomic Absorption Spectrophotometer

ANOVA- Analysis of Variance

APHA- American Public Health Agency

DL- Detection Limit

DO- Dissolved Oxygen

EC- Electrical Conductivity

EU- European Union

FAAS - Flame Atomic Absorption Spectrophotometer

GPS - Global Positioning System

HDPE- High-Density Polyethylene bottle

LCS-Laboratory Control Sample

LFB- Laboratory Fortified Blank

LOD-Limit of Detection

LOQ- Limit of Quantification

MAL-Maximum Permissible Limit

MDL-Maximum Detection Limit

MRL- Minimum Reporting Level

NGL- No Guide Line

NTU- Nephelometric Turbidity Unity

OS- Saturated Oxygen

QC- Quality Control

RSD- Relative Standard Deviation

SD – Standard Deviation

SWS - Spring Water Sample

TSS- Total Suspended Solids

USEPA- United State Environmental Protection Agency

UV-Vis spectroscopy - Ultraviolet and Visible Spectroscopy

WHO-World Health Organization

## **Abstract**

The study investigated the physico-chemical parameters and the level of some heavy metals in different protected spring water samples of Jimma town, Oromia regional state, Southwestern Ethiopia. For this purpose, eight different spring water samples were randomly collected to serve as the subject of the study. Physico-chemical parameters and heavy metals were determined using standard analytical procedures. The result of the physicochemical analysis were obtained in the following range; pH (6.48-8.30), temperature (21.60-23.60 °C), conductivity (57.80-638.00 µS/cm), dissolved oxygen (1.09-6.70 mg/L), turbidity (1.14-27.70 NTU), total suspended solids (0.385-2.80 mg/L). The turbidity of three of spring water samples (SWS 05, SWS 06 and SWS 08(37.5 %)) were found to be above the permissible limit set by WHO drinking water standards, which is  $27.7\pm 0.2$ ,  $23.6\pm 0.2$  and  $7.86\pm 0.01$  respectively. The electrical conductivities of three of spring water samples (SWS 01, SWS 02 and SWS 04(37.5 %)) were found to be above the permissible limit set by WHO drinking water standards, which is  $638\pm 1$ ,  $410\pm 12$  and  $394\pm 7$  respectively. The range of concentration of nitrate and phosphate were found to be 13.28 to 281.11 and 0.01 to 0.10 mg/L respectively. The concentrations of heavy metals (mg/L) in the samples were found within the following ranges; Pb (0.002-0.0615), Cd (0.0015-0.0235), and Cr (VI) (Not detected - 0.052). The level of lead of four of spring water samples (SWS 01, SWS 04, SWS 05 and SWS 08(50 %)) were found to be above the permissible limit set by WHO drinking water standards. The level of Cr (VI) of one spring water sample (SWS 04) was found above the permissible limit set by WHO drinking water standards. Therefore, although, all of the sampled spring waters were protected; they need continuous monitoring and needs solutions for the parameters which are above permissible limit set by EU, USEPA and WHO.

**Keywords:** Heavy metals, Physico-chemical parameter, Physico-chemical analysis, spring water, Spring water sample

# 1 INTRODUCTION

## 1.1 Background of the study

Water is one of the essentials that support all forms of plants and animals life<sup>1</sup> and it is generally obtained from two principal natural sources; surface water (lakes, rivers, streams, etc.) and ground water (borehole and well water)<sup>2,3</sup>. More than one billion people in the world do not have suitable drinking water, and two to three billions lack access to basic sanitation services. About three to five millions die annually from water-related diseases<sup>4</sup>. In the hydrological cycle, less than 0.1% of the metals are actually dissolved in the water and more than 99.9 % are stored in sediments and soils<sup>5,6</sup>. Heavy metals are among the major pollutants of water sources<sup>7</sup>.

Anthropogenic activities like mining, ultimate disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates<sup>8</sup> from different industries, e.g. tannery, steel plants, battery industries, thermal power plants, etc. and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing the threat on human beings<sup>9,10</sup> and sustaining aquatic biodiversity<sup>11,12</sup>.

On the global scale, agricultural, industrial, and municipal activities have all resulted in surface and groundwater pollution by a variety of contaminants<sup>13-19</sup>. Specifically, trace metal contamination of water has emerged as a serious health issue highlighted<sup>20-22</sup>. Metals such as cadmium, chromium and lead may produce toxic effects when their levels exceed certain limits in organisms.

Since springs principal water source is groundwater, many springs have water that is crystal clear, yet rich with dissolved nutrients and gases<sup>23</sup>. In earlier times springs were central to the establishment of local communities; both in providing continuous water supplies for individual homes and farms and as the center piece of small towns that developed around the larger springs. Even today, spring flow continues to provide potable water for a substantial number of people and animals within the watershed<sup>24</sup>. Particularly for developing countries which have an access, naturally occurring springs are an important source of drinking water. Unlike wells, which may

be owned and controlled privately; springs are generally community-owned and community-managed. Thus, they give a sense of a “common” resource; therefore, groundwater which is shared through a common mechanism is a spring<sup>25</sup>. Some springs forms small ponds where animals drink and people may well also dig water from there. Others flow as small streams in valleys and can be traced back to the source<sup>26</sup>. Geology, topography and climate are factors which influence the amount of water that occurs as surface flow versus the amount that infiltrates into the ground water as recharge to ground water. All these three factors govern how the sub surface flow system develops and ultimately where the springs occur<sup>27</sup>.

In general, spring water can be of good quality; therefore, most of the time pathogenic contamination is unlikely if the source meets certain criteria. These include the thickness of the soil layer, the type of soil and the velocity of infiltration of the surface water. The type of soil determines the speed of the flow through the voids in the soil and so influences the purification mechanisms and the concentration of suspended solids. If the soil layer is not thick enough, any human activity should be restricted or even forbidden in the catchment area. Otherwise, local farmers may be allowed to conduct some agricultural activities in the catchment area under some restrictions such as no use of artificial fertilizers or harmful chemicals<sup>28</sup>.

Springs belong to very important abiotic elements of the environment, especially in legally protected areas<sup>29</sup>. A decrease in the number of springs or the drop in their discharge, as well as disadvantageous changes in chemistry and quality of spring waters, indicate degradation of the environment. The quality of groundwater is therefore, controlled by combined interactive natural and anthropogenic factors. Protected springs are commonly characterized by the area where the water sources are built by concrete and fence surrounding the area. Of course, each spring is unique and all designs need adapting to suit the type of spring and the topography. The major parts of the construction are the permeable construction and the dam. The permeable construction is a package of filter material made of rocks, stones and gravel that allows water to drain into the supply pipes. The barrage can be a concrete dam or a stone masonry construction controlling the drain and directing water into the supply pipes<sup>30</sup>.

Protection of the catchment has two main objectives; which is to improve the recharge of the aquifer, and to prevent contamination of the groundwater. Catchment protection; therefore,

involves planning, implementation and motivation to refrain from or substantially reduce human and economic activities that could cause adverse effects on the quality and quantity of the water from the spring. Production of feed grass and crops not requiring application of chemicals are permitted, but the feeding of animals on this fodder grass should be outside the catchment area. The immediate area around the spring (at least with a 50 m radius) must be fenced with barbed wire or an alternative barrier. In this area definitely no human activities such as farming, grazing and hunting are allowed. Protection activities here include soil conservation, erosion control, drainage work and planting of trees, shrubs and grasses<sup>30</sup>.

Spring water, now days whether by nature or human activities are sources of various chemical compositions. Bicarbonate, Chloride and Ca/(Ca+Mg) which are formed from dissolution of dolomite and pure calcite, respectively are among the major analytes found in spring water. Sulfate ( $\text{SO}_4^{2-}$ ) and Nitrate ( $\text{NO}_3^-$ ) which are resulted from dissolution of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or anhydrite ( $\text{CaSO}_4$ ), and oxidation of ammonium or other nitrogen compounds respectively are also among anions in spring water. High level nitrite- nitrogen, ammonia- nitrogen and phosphate which may be attributed to agricultural activities are explained in different research works as chemical constituents' of spring water as well. Total organic carbon (TOC), silicate due to weathering and metals like lead, arsenic, chromium, cadmium, potassium, sodium, barium, cobalt, copper, zinc, lithium, mercury, aluminum and iron are introduced as pollutant or weathering of rocks determined in different forms and reported afterwards as components exist in the spring water<sup>31, 32</sup>.

## 1.2 Statement of the problem

Approximately, two thirds of the world's populations obtain water supply from ponds, wells, springs, rivers, rains etc<sup>33</sup>. But these water sources are vulnerable to different pollutants such as heavy metals such as Pb, Cd, Cr, As, which are toxic to human beings<sup>34, 35</sup>. In Ethiopia, the main source of water supply for both urban and rural communities is the underground water which accounts to 70 % of the total water supply of the nation<sup>36</sup>. Similarly Jimma town and its surrounding communities get water supply for drinking, home consumptions as well as other activities from surface water, springs and well-water<sup>37</sup>. The surface water coverage is estimated to 64 % in the former 46 km<sup>2</sup> town coverage whereas the remaining 36 % is from the well-water and spring water<sup>37</sup>.

In addition, recently, the total area of the town has been expanded to rural kebeles and thus increased from 46 km<sup>2</sup> to the 100.2 km<sup>2</sup>. Due to this expansion about 54.2 km<sup>2</sup> new area of the town uses spring water and well water for drinking, other domestic and agricultural purposes<sup>17</sup>. Moreover, majority of the surrounding communities of the town also do not have access to clean water supply and thus they use well, stream and river waters<sup>39</sup>. As a result, the surrounding communities of the town might have been highly exposed to water borne diseases caused by uncounted various solid and liquid waste disposals<sup>40</sup>. In the study area, based on the 2007 population census<sup>41</sup>, Jimma town population is estimated to be around 229, 857. As a growing town, the population is increasing from time to time. This may result in associated water shortage and use of unsafe water supplies as it was the case in Addis Ababa<sup>42</sup>. Therefore, assessing the magnitude of pollutants in spring water supply that has been used by the community for different purposes is important to improve the quality of supply and utilization of water resource of the town.

## 1.3 Objectives of the Study

### 1.3.1 General Objective

- ✚ To investigate the physico-chemical parameters and the level of some heavy metals in spring water of Jimma town.

### 1.3.2 Specific objectives

- To analyze the physicochemical parameters like pH, temperature, turbidity, dissolved oxygen, total suspended solid, electrical conductivity of protected spring water samples of Jimma town
- To determine the concentration of some selected heavy metals in the protected spring water samples of Jimma town using FAAS
- To determine the concentration of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and Cr(VI) in the protected spring water samples of Jimma town using Uv-Vis spectrometry
- To compare the determined water quality parameters with the International and National standards as well as reported literature values

## 1.4 Significance of the Study

A number of protected and unprotected spring water can be contaminated by toxic pollutants such as heavy metals, nitrates, phosphates and thus influencing its physico-chemical parameters. Hence, this study could indicate the level of these contaminants in spring water from which residents of Jimma town access water for various uses. Further, it may provide some information about the source of these contaminants in the spring water of the town. Therefore, the finding of the study may also be used as a baseline resource for other researchers who want to study the spring water found in Jimma town.



## **2 REVIEW OF RELATED LITERATURE**

Ethiopia's development is seriously influenced by complex water resources legacy and lack of access to clean water and management of the water resources<sup>43</sup>. Clean water supply and appropriate sanitation are the most essential components for healthy life. The provision of drinking water with adequate sanitation facilities to both the rural and the rapidly expanding urban populations can reduce mortality rates that come from water borne and other water related diseases such as cholera, diarrhea and malaria<sup>33, 43</sup>. Although, there are diversified water resources in the country, large proportion of the population does not get access to clean drinking water. As a result, poor hygiene, cholera outbreak, dehydration and high child mortality are observed throughout the nation<sup>33</sup>.

Water can be contaminated by natural and anthropogenic sources and thus the physical and chemical properties of the water may vary over time and by location<sup>44, 45</sup>. These contaminants include different naturally occurring chemicals and anthropogenic chemicals emerging from agricultural farmlands, human dwellings and industry. Chemicals used in water treatment such as pesticides which are used in water for public health purposes; cyan bacterial toxins and other contaminants derived from biological sources are also sources of water contaminants<sup>46, 47</sup>.

In Ethiopia, the major sources of drinking water, for the vast majority of the rural population and residents of many small towns are unprotected surface waters as well as underground water<sup>48, 49</sup>. The health risks of the water obtained from such sources are significant as they are exposed to the earlier mentioned contaminations sources<sup>49</sup>. Use of contaminated drinking water may cause adverse health effects over prolonged periods of exposure. Therefore, determination of the level of water contaminants, such as heavy metals, that have cumulative toxic effect on the users' should be continually monitored<sup>43</sup>.

### **2.1 Sources of trace heavy metals**

Water is the most essential basic necessity of life. However, pure water needed for human consumption does not always occur in nature, due to the presence of dissolved or suspended impurities in most natural water bodies. Water pollution occurs when a body of water is adversely affected due to the addition of large amounts of materials to the water. When it is unfit for its intended use, water is considered polluted. Other problem of water pollution is

contamination due to urbanization; this is a rising topic worldwide. The metal concentrations increased with increasing intensity of urban dwellers, but site specific factors, such as point sources, are responsible for the occurrence of the highest metal concentrations<sup>50</sup>.

## **2.2 Toxicity, role and analysis of trace heavy metals**

Heavy metals significantly contribute to human environment pollution due to the impossibility of their biodegradation, and because some of them have cumulative toxic properties<sup>51</sup>. Due to the high toxicity and stability of Pb, Cd, and Cr, it is necessary to determine their content in materials, food, water and other samples to estimate their contamination level.

### **2.2.1 Lead**

Lead has a potential to compete with the essential metals in the human body (Ca, Fe, Cu, Zn). Therefore, based on its physico-chemical characteristics,  $Pb^{2+}$  ions can replace  $Ca^{2+}$  ions isomorphically as part of hydroxyapatite, which leads to the accumulation of this metal in mineral tissue, the teeth and bones. During physiological processes of bone tissue remodeling, part of the  $Pb^{2+}$  ions, by migration through the oral and other biological fluids, reach other remote organs, hence the brain, kidneys, and the liver<sup>52, 53</sup>. Everyone is exposed to trace amounts of lead through air, soil, household dust, food, drinking water and various consumers. Inorganic lead arising from a number of industrial and mining sources like pigments, anticorrosion coatings, lead smelter, alloys, and batteries occurs in water in the +2 oxidation state<sup>54, 55</sup>.

Lead is easily deposited in blood, kidney, reproductive system, nervous system and brain so as results fatal diseases. Acute lead poisoning in humans causes severe damage in the kidneys, liver, brain, reproductive system and central nervous system, and even causes death. Its mild poisoning cause anemia, headache and sore muscles and the victim may feel fatigued and irritable. Chronic exposure to lead causes nephritis, scarring and the shrinking of kidney tissues<sup>56, 57</sup>. Moreover, lead and its compounds are reasonably anticipated to be human carcinogens based on limited evidence of carcinogenicity from studies in humans and sufficient evidence of carcinogenicity from studies in experimental animals<sup>58</sup>. Most victims of lead poisoning are children with low socioeconomic status, such as children living in slums<sup>48</sup>. Lead exposure accounts for about 1 % of the global burden of disease and sympathetically most exposure affects children in developing countries. About 15-20 % mental retardation could be caused by

exposure to lead; likewise, high blood lead levels in children may cause permanent deficiencies in growth<sup>48, 59</sup>.

### **2.2.2 Cadmium**

Cadmium is usually present as complex oxides, sulfides, and carbonates in zinc, lead and copper ores. Cadmium in several aspects is similar to zinc and therefore, it is always associated with zinc in mineral deposits. Cadmium is extremely toxic to most plants and animal species particularly in the form of free cadmium ions. The major sources of cadmium include metallurgical industries, municipal effluents, sewage sludge and mine wastes, fossil fuels and some phosphorus containing fertilizers. Cadmium can potentially harm human health depending upon the form of cadmium present, the amount taken in, and whether the cadmium is eaten or breathed. For example, if the levels are high enough, the cadmium in the kidney will cause kidney damage<sup>27</sup>.

### **2.2.3 Chromium**

Chromium is an essential nutrient required for normal sugar and fat metabolism and works primarily by potentiating the action of insulin. It is present in the entire body but with the highest concentrations in the liver, kidneys, spleen and bone. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water. The maximum concentration of Cr (VI) permitted in potable water is 0.05 mg L<sup>-1</sup>. Hexavalent compounds have been shown to be carcinogenic by inhalation and are corrosive to tissue. The chromium guidelines for natural water are linked to the hardness or alkalinity of the water (i.e., the softer the water, the lower the permitted level for chromium). The most important application of chromium in the metallurgic industry is its use as an alloying element in steels<sup>60</sup>.

## **2.3 Analysis of the Physico-Chemical parameters**

### **2.3.1 Color, Odor and Taste**

Color may be indicative of dissolved plant material or the presence of dissolved metals. Odors, which can be caused by a wide variety of dissolved substances, are useful indicators of water quality even though odor-free water is not necessarily safe to drink. Most water quality standards say generally that lakes, streams and other waters must be free from objectionable tastes, odor or colors, regardless of their use. But when the waterway is also a drinking water source, these characteristics become much more important because unpleasant levels can cause a community to reject the source as drinking water or require additional, expensive drinking water treatment to remove tastes, odors or colors<sup>28</sup>.

### **2.3.2 Temperature**

Cold water has a greater natural affinity for oxygen molecules than warm water. This relationship between temperature and dissolved oxygen causes a reduction in dissolved oxygen as the temperature of a fresh water body increases. This in turn affects physicochemical and biological processes in water bodies<sup>61</sup>. Oxygen is more soluble, meaning that it dissolves more readily in cold than in warm water. Hence, cold water has a greater natural affinity for oxygen molecules than warm water<sup>62</sup>. One of the key signs of a good spring is that the water maintains a constant temperature throughout the day. This temperature is just below the average air temperature. The water should also be colorless. Variation of water temperature during the day and coloration of water shortly after rains are indications of a poor quality spring source.

### **2.3.3 pH**

pH is a very important variable in water quality assessment as it influences biological and chemical processes. Acids and base can affect the pH of a water body and may eliminate those aquatic organisms that are pH change intolerant. Besides, a reduction in pH will increase the mobility of trace metals and makes them bioavailable for organisms<sup>63</sup>.

### **2.3.4 Turbidity**

Turbidity measures water clarity or the ability of light to pass through water. Water that has high turbidity appears cloudy or opaque. The adsorption capacity of suspended particulates can lead to the entrapment of undesirable compounds (both inorganic and organic); as such, turbidity can bear an indirect relationship to the water quality parameters aimed at monitoring such compounds. High turbidity can cause increased water temperatures because suspended particles absorb more heat and can also reduce the amount of light penetrating the water. The suspended particles also help the attachment of heavy metals and many other toxic organic compounds and pesticides<sup>27</sup>.

### **2.3.5 Electrical Conductivity**

Electrical conductivity (EC) is an indirect measure of water salinity, and one of the most common and convenient methods used to test water. It is significantly affected by the temperature, so all results should be normalized to a standard temperature of 25 °C. The EC is also strongly dependent upon the ionic composition of water. Chloride and sodium ions are commonly the main ions influencing groundwater Electrical conductivity. Other ions that contribute to salinity are carbonates, sulfates, magnesium, calcium and potassium<sup>64</sup>.

### **2.3.6 Dissolved Oxygen (DO)**

Dissolved Oxygen is the concentration of molecular oxygen dissolved in water. Units are typically reported in milligrams per liter (mg/L) or percent (of air saturation). DO test is the basis of biological oxygen demand test which is an important parameter to evaluate pollution potential of wastes. Measurement of DO is critical to the scientific understanding of the potential for chemical and biochemical processes in groundwater. Water that enters groundwater systems as recharge can be expected to contain oxygen at concentrations similar to those of surface water in contact with the atmosphere. Organic matter or oxidizable minerals present in some aquifers rapidly deplete the dissolved oxygen. Therefore, in aquifers where organic materials are less plentiful, groundwater containing measurable concentrations of DO (2-5 mg L<sup>-1</sup>) can be found<sup>54</sup>.

### **2.3.7 Total Suspended Solids (TSS)**

TSS is solid materials, including organic and inorganic, that are suspended in the water; which would include silt, plankton and industrial wastes. Source of total suspended solids include erosion from urban runoff and agricultural land, industrial wastes, bank erosion, bottom feeders, algae growth or wastewater discharges. High concentrations of suspended solids can lower water quality by absorbing light. Waters then become warmer and lessen the ability of the water to hold oxygen necessary for aquatic life<sup>65</sup>.

### **2.3.8 Orthophosphate**

Phosphorus stimulates explosive blooms of aquatic algae, including especially dangerous cyanobacteria (blue-green algae) that produce toxins which can be deadly to pets, livestock, wildlife and people. Toxins produced by cyanobacteria can harm the nervous system, cause stomach and intestinal illness and kidney disease, trigger allergic responses and damage the liver. Even after a brief exposure, cyanobacteria toxins can cause skin rashes, eye irritation and breathing problems<sup>66</sup>.

### **2.3.9 Nitrate**

Nitrogen, found in commercial fertilizers and manure, is applied in many different chemical forms. Bacteria can convert all of them to nitrate, a form of nitrogen that can be taken up by plant roots. Nitrate is very soluble in water and is easily carried from farm fields into streams and rivers. It is the most common form of nitrogen in surface and groundwater, is directly toxic to human health. Infants who drink water with high nitrate levels can develop an acute, life-threatening blood disorder called blue baby syndrome. High nitrate levels in water can also affect thyroid function in adults and increase the risk of thyroid cancer<sup>66, 67</sup>.

## 3 MATERIALS AND METHODS

### 3.1 Chemicals and Materials

#### 3.1.1 Chemicals

The chemicals used for this study were: Sulfuric acid,  $\text{H}_2\text{SO}_4$  (98 %, UNI-CHEM, Germany), Hydrochloric acid,  $\text{HCl}$  (37 %, Riedel-deHaën, Germany), Nitric acid,  $\text{HNO}_3$  (Wardel Chemicals lmtd, 69 %), Potassium nitrate,  $\text{KNO}_3$  (Riedel-deHaën), Sodium hydroxide,  $\text{NaOH}$  (Alphachemika, 98 %), Potassium dihydrogen orthophosphate,  $\text{KH}_2\text{PO}_4$  (NICE, 99 %), Ammonium molybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (Riedel-deHaën), Lead nitrate,  $\text{Pb}(\text{NO}_3)_2$  (FINKEM, 99 %), Cadmium Chloride,  $\text{CdCl}_2$  (Aldrich, 99.5 %), Potassium chloride,  $\text{KCl}$  (Supertek, 98 %), suspension of Formazin (hydrazine sulphates),  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$  (BDH Chemicals), Hexamethylenetetramine solutions,  $\text{C}_6\text{H}_{12}\text{N}_4$  (Riedel-deHaën), Barium chloride,  $\text{BaCl}_2$  (Supertek, 98 %), Stannous chloride,  $\text{SnCl}_2\cdot\text{H}_2\text{O}$  (Wardel Chemicals lmtd, 78%), Glycerol,  $\text{C}_3\text{H}_8\text{O}_3$  (BDH chemicals, 97 %), Phenolphthalein indicator,  $\text{C}_{20}\text{H}_{14}\text{O}_4$  (Ludgate), White phenol,  $\text{C}_6\text{H}_5\text{OH}$  (UNI-CHEM), Ethylenediaminetetraacetate, EDTA,  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$  (Aldrich), Ammonium hydroxide,  $\text{NH}_4\text{OH}$  (Mistral, 35 %), Potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$  (Supertek, 99.5 %), Phosphoric acid,  $\text{H}_3\text{PO}_4$  (Supertek, 85 %), Silver sulfate,  $\text{Ag}_2\text{SO}_4$  ( ), 1,5-diphenylcarbazine,  $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$  (Aldrich), Acetone,  $\text{C}_3\text{H}_6\text{O}$  (BDH Chemicals), Potassium permanganate,  $\text{KMnO}_4$  (Cemfin, 90 %).

#### 3.1.2 Materials

The materials used for this study were: volumetric flasks, conical flasks, beakers, droppers, safety goggles, pipettes, nitrile gloves, GPS, scissors, polyethylene plastic bottles, water bath, micropipettes, round bottom flask, graduated measuring cylinders, spatula, evaporating dish, glass rod, porcelain dish, 0.45 micron micropore membrane filter and Whatmann No. 30 filter paper, stopwatch, cuvette, glass fiber filter disk, suction pump, membrane filter funnel, washing bottle, hot plate, refrigerator, oven, brown bottle, desiccators.

### **3.2 Instruments**

The instruments used for this study were: Flame Atomic Absorption Spectroscopy (FAAS) (AA320N), UV-Visible Spectrophotometer (Model DR 5000, Hach USA), pH meter (HANNA instruments, pH 211), Electronic balance that can measure up to 110 g (Model AFP-110L, ADAM, China), and Multimeter parameter probe (HATCH-HQ4OD).

### **3.3 Solution preparation**

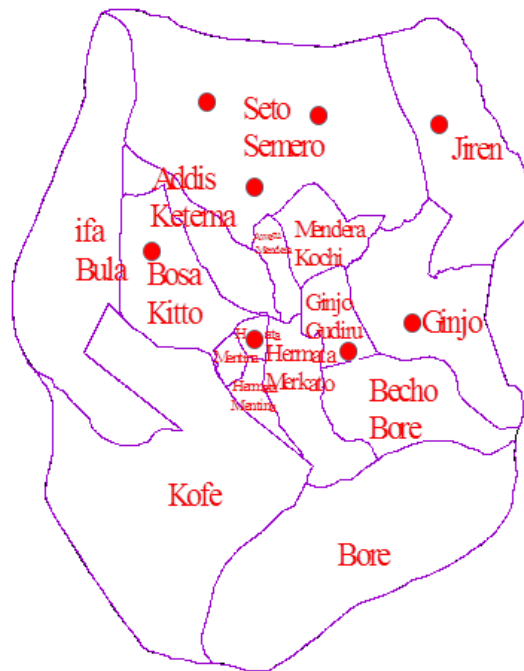
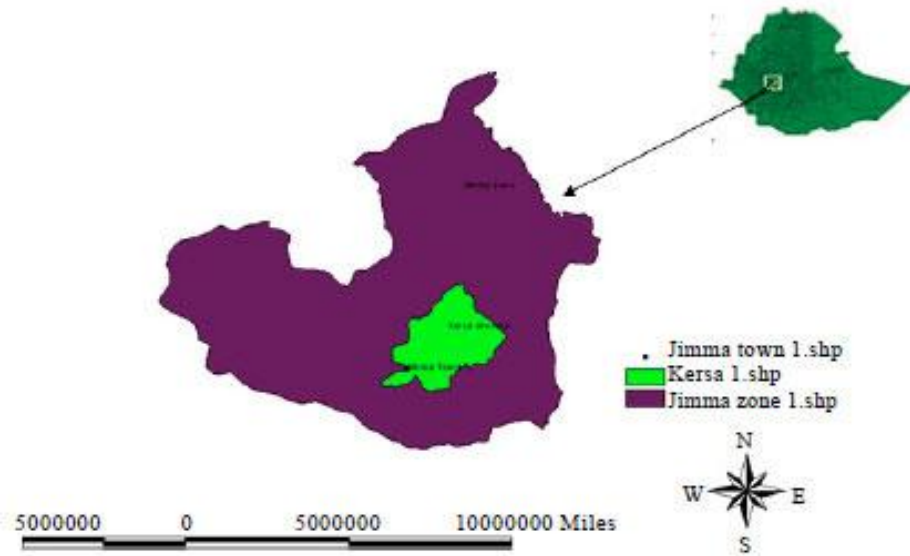
Intermediate working standard solutions containing 50 ppm Pb, Cd, Cr (VI),  $\text{PO}_4^{3-}$ , and  $\text{NO}_3^-$  was separately prepared by taking 5 mL of their stock solutions; which was 1000 mg/L and diluting in to 100 mL with deionized water. Working standard solutions of each these analytes was then prepared by serial dilution from the intermediate solution.

### **3.4 Sampling**

#### **3.4.1 Description of the sampling sites**

Spring water sample was collected from different parts of Jimma town, found 346 Km from Addis Ababa, which is located  $7^{\circ} 40' \text{N}$  latitude and  $36^{\circ} 60' \text{E}$  longitudes, and altitude ranging from 1,700 - 1,750 m, with the highest altitude around king Aba Jifar II palace, as well as the lowest around Aba Jifar Airport area<sup>68</sup>. According to the master plan of the town, the total area of land town is 4623 Hectares ( $46.23\text{km}^2$ )<sup>59</sup>.





● Sampling sites

**Figure 1:** Spring water sampling sites, Jimma town, Jimma zone, May, 2014

Mentina-Key Meskel, N07°39.983':E036°49.464'



ober-Key Meskel, N07°40.630':E036°50.



Sarsefer-Minch, N07°41.625':E036°49.276'



Furustale-Minch, N07°41.374':E036°49.808'



Seto-Key Meskel, N07°41.816':E036°50.105'



Aba Arebu, N07°41.650':E036°50.546'



ma, N07°40.033':E036°51.478'



Motor Buwanbuwa-N07°41.445': E036°51.727'



**Figure 2:** The representative pictures of spring waters of sampling site; Jimma town, May, 2014

**Table 1:** Specific sampling sites of the spring waters, Jimma town, May, 2014

<b>Sampling sites</b>	<b>Sampling sites code</b>	<b>Altitude(m)</b>	<b>North-direction</b>	<b>East-direction</b>
Mentina-Key Meskel	SWS 01	1716	N-07 <sup>0</sup> 41.445'	E-036 <sup>0</sup> 51.727'
Agarober-Key Meskel	SWS 02	1713	N-07 <sup>0</sup> 40.630'	E-036 <sup>0</sup> 50.017'
Sarsefer-Minch	SWS 03	1718	N-07 <sup>0</sup> 41.625'	E-036 <sup>0</sup> 49.276'
Furustale-Minch	SWS 04	1735	N-07 <sup>0</sup> 41.374'	E-036 <sup>0</sup> 49.808'
Seto-Key Meskel	SWS 05	1743	N-07 <sup>0</sup> 41.816'	E-036 <sup>0</sup> 50.105'
Aba Arebu	SWS 06	1740	N-07 <sup>0</sup> 41.650'	E-036 <sup>0</sup> 50.546'
Tulema	SWS 07	1724	N-07 <sup>0</sup> 40.033'	E-036 <sup>0</sup> 51.478'
Motor Buwanbuwa	SWS 08	1766	N-07 <sup>0</sup> 41.445'	E-036 <sup>0</sup> 51.727'

**SWS –spring water sample****3.4.2 Sample collection and preservation**

The spring water samples were collected from the identified eight sampling sites, from May 3-5, 2014(25-27/8/2006 E.C), using grab sampling method<sup>69</sup>. During sampling, the sampling bottles and their caps were repeatedly rinsed with the water to be sampled. Each of spring water samples were acidified to pH < 2 with 2 mL concentrated HNO<sub>3</sub> per liter for lead and cadmium. The samples of chromium (VI) were treated with 5 mL mixture of Na<sub>2</sub>CO<sub>3</sub> and NaOH to raise their pH 9.5 or higher and the samples collected for nitrate, orthophosphate were kept without making any pretreatment. Afterwards, the collected samples were transported to the laboratory and then stored in refrigerator below 4 °C until time of analysis, in order to minimize changes of the physicochemical characteristics of the samples<sup>70</sup>.

### **3.5 Sample preparation procedure**

#### **3.5.1 Digestion of water samples for Pb, Cd and Cr (VI) determination**

For the determination of Pb and Cd, 100 mL of the acidified water sample was taken into 200 mL beaker. After 5 mL concentrated HNO<sub>3</sub> was added, the beaker was covered with watch glass and the content was then boiled (digested on hot plate at 95<sup>0</sup>C for 3 h, until it was reduced to about 20 mL. The obtained 20 mL digested sample was filtered using Whatman filter paper and transferred to 100 mL volumetric flask and then, its volume was adjusted to the mark using distilled water. Finally, the concentrations target analytes in the digested samples were determined by FAAS using external calibration curve.

Cr (VI) was determined using reported methods<sup>71, 72</sup>. In this procedure 100 mL of the water sample was taken into 200 mL beaker and was then slowly heated to boiling on the hot plate until the sample volume was reduced to approximate 20 mL. After cooling, 20 mL of the digested sample was transferred to 25 mL volumetric flask and then, 2 mL of 6N H<sub>2</sub>SO<sub>4</sub>, and 0.5 mL of 0.1 M biphenyl carbazide was added to it. Then, the remaining volume was adjusted to using deionized water. Finally, the concentration of total chromium in prepared sample was carried out using UV-Vis spectrophotometer at 540 nm.

#### **3.5.2 Water sample preparation for determination of orthophosphate and nitrate**

Orthophosphate was determined by using reported methods<sup>73, 74</sup>. 100 mL of the water sample was taken into volumetric flask and a drop of 0.2 M, of phenolphthalein indicator was added to check the basicity of the sample. Then, after adding 4 mL of 0.1 M ammonium molybdate, the content was manually shaken thoroughly to mix the solution. Subsequently, 10 drops of 0.1M, of stannous chloride was added and was again shaken to mix the solution. Blank water samples were also prepared by the same procedure used. Similarly, nitrate was determined using reported method<sup>75</sup>. In this procedure water sample was prepared as follows: 100 mL of the water sample was taken and 1mg/mL Ag<sub>2</sub>SO<sub>4</sub> solution was then added to test the presence of the chloride ions. Then, after filtering the resulting solution, 20 mL of the filtrate was transferred into evaporating dish and boiled in the water bath to evaporate into dryness. Subsequently, 2 mL of 0.7 M phenoldisulfonic acid was added to dissolve the resulting residue and then, the hot solution was

kept for about 5 minutes until it was dried to solid. The obtained solid residue was dissolved in 20 mL distilled water and then, 7 mL of 12 N KOH was added in stepwise with continuous stirring until yellow color was developed. The solution was then quantitatively transferred to 50 mL volumetric flask and its volume was adjusted to the mark with distilled water. Finally, the quantitative determination of nitrate-nitrogen concentration in the target sample was performed using UV-Vis spectrophotometer at wavelength of 410 nm using external calibration curve.

### 3.5.3 Water sample preparation for total suspended solids

In order to determine, TSS, 100 mL of water sample was taken and centrifuged for 30 minutes and filtered using a glass fiber filter which was previously dried for an hour at 103 °C in oven. The residue left on the glass fiber filter was then dried for an hour in oven at 103°C. Eventually, the amount of TSS in the water sample was determined by gravimetric method<sup>76,77</sup>.

$$TSS = \frac{A - B}{\text{sample volume in ml}} \times \frac{1000mg}{l} \quad [1]$$

A= weight of filter + dried residue in mg,

B= weight of filter in mg.

### 3.5.4 Preparation of laboratory control samples

The laboratory control samples (LCS) was prepared by spiking distilled water with a known amount of the target analytes. Firstly, certain amount of distilled water was taken in to 100 mL volumetric flask and then spiked with 2 mL of mixed standard solution containing 0.5 mg/L Pb, 0.5 mg/L Cd, 0.02 mg/L Cr( VI), 0.2 mg/L PO<sub>4</sub><sup>3-</sup> and 0.6 mg/L NO<sub>3</sub><sup>-</sup>. Finally, the LCS was analyzed for each analytes as it has been done for respective samples.

## **3.6 Water sample analysis for physico-chemical Parameters**

### **3.6.1 pH Determination**

pH of the water was determined with the help of pH probe of multi meter.

### **3.6.2 Electrical Conductivity**

The conductivity of water was determined with the help of conductivity probe multi meter by immersing it to the beaker contain the sample and reading was made from the display which expressed in terms of  $\mu\text{S}/\text{cm}$ .

### **3.6.3 Turbidity Determination**

The sample was agitated gently and waited until air bubbles disappeared. Then the well-mixed sample was poured into cell. Finally, turbidity was directly read from instrument display.

### **3.6.4 Temperature Determination**

Temperature measurement was made by taking a portion of the water sample with a beaker (about 1L) and immersing the probe into it for about 2 minutes (till the reading stabilized) and readings were taken then expressed in  $^{\circ}\text{C}$  in due course<sup>78</sup>.

### **3.6.5 DO Determination**

The instrument which was used to measure DO has a membrane electrode which possesses a sensing element protected by an oxygen-permeable plastic membrane that served as a diffusion barrier against impurities. Under steady conditions, the electric current read is directly proportional to the DO concentrations or electric current produce during measurement is directly proportional to the activity of molecular oxygen. Therefore, the calibrations were carried out after the electrode was dipped into the sample, and this electric current reads then it was noted as % saturation and  $\text{mg}/\text{L}$ <sup>78</sup>.

### 3.7 Water sample analysis for Heavy Metals

#### 3.7.1 Analysis of Lead and Cadmium by FAAS

The analysis of lead and cadmium were done by using FAAS, based on the sample being aspirated into the flame and atomized when the AAS's light beam was directed through the flame into the monochromator, and onto the detector that measures the amount of light absorbed by the atomized element in the flame. The concentration of the heavy metals was determined by using five points calibration curve from which the working standards prepared using 1000 ppm stock solution, and ran the analysis in FAAS<sup>79</sup>.

**Table-2:** Parameters for FAAS at which lead and cadmium ions were analyzed

Element	Lamp current (mA)	Fuel	Flame type	Wave length (nm)	Slit width (nm)
Lead	4	C <sub>2</sub> H <sub>2</sub> - Air	Oxidizing	283.3	0.7
Cadmium	4	C <sub>2</sub> H <sub>2</sub> - Air	Oxidizing	228.8	0.7

Finally, concentration of lead and cadmium were calculated as:

$$\mu g \frac{metal}{L} = C \times DF \quad [2]$$

C= metal concentration as read directly from the instrument or from the calibration curve,  $\mu g/L$ , and DF= dilution factor.

$$DF = \frac{Final\ volume\ of\ diluted\ aliquote}{volume\ of\ aliquote\ taken\ for\ dilusion} \quad [3]$$

#### 3.7.2 Analysis of Cr (VI)

Cr (VI) was analyzed using Diphenylcarbazide method by UV-Vis Spectrophotometer.

### 3.8 Method Validation

#### 3.8.1 Calibration curve linearity

For quantitative determination of the target analytes external calibration curve was used. For each analytes (i.e., Pb, Cd, Cr (VI),  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ) a series of five concentrations were used for constructing the calibration curves and for each 0.994 - 0.999 coefficients of determinations were obtained. The concentration of the analytes was determined using the linear equation obtained from the calibration curves.

#### 3.8.2 Determination of method detection limit

Method detection limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99 % confidence that the analyte concentration is greater than zero. In this study MDLs were determined using blank sample, which was, free from the analyte of interest<sup>80</sup>. Accordingly, for each analytes seven LCSs were measured and the desired MDLs were calculated as follows.

$$S = \left[ \sum \frac{(x - \bar{x})^2}{(n-1)} \right]^{\frac{1}{2}} \quad [4]$$

Where, S is standard deviation

$$\text{MDL} = (t) \times (s) \quad [5]$$

S = standard deviation of the replicate analyses, t = value appropriate for a 99 % confidence level and n-1 degrees of freedom (t = 3.14 for seven replicates)



### 3.8.3 Precision and recovery studies

Precision study was assessed in terms of percent relative standard deviation (% RSD) by the analyzing of blank samples (n=7) spiked with known concentration<sup>68</sup>.

$$\%RSD = \frac{\textit{Standard Deviation of measured Concentration}}{\textit{Average Concentration}} \times 100 \quad [6]$$

In the same way, accuracy was assessed by % R using blank samples (n=7) which was spiked with known concentration and calculated as follow.

$$\%R = [(C_{sp} - C_{usp}) \times 100] / C_{an} \quad [7]$$

Where, % **R** is percent recovery of blank spiked, **C<sub>sp</sub>** is concentration of spiked sample and **C<sub>usp</sub>** is concentration of unspiked sample and **C<sub>an</sub>** concentration of analyte spiked.

## 4 RESULTS AND DISCUSSION

### 4.1. Determination of Pb, Cd, Cr (VI), NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>

Quantitative determinations of the target analytes were performed using FAAS for (Pb and Cd) and UV-Vis spectrophotometer for [Cr (VI), NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>] based on external calibration curves. For construction of calibration curves a series of standard solutions containing five different concentrations of the analytes were prepared in distilled water and their absorbance's were then measured and used to construct the curves as the function of the target analyte concentrations. The obtained calibration curves were exhibited good linearity with coefficient of determinations, R<sup>2</sup> of 0.996 to 0.999.

The concentrations of the analytes in the spring water and in method blank samples were then determined using the linear equation obtained from the curves. MDL of the analytes were determined using reagent water or method blank, in which seven (n=7) measurements were used for the determinations. Analytical performance characteristics of the method for determination of Pb, Cd, Cr(VI), NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> are presented in Table 3 and Table 4.

### 4.2 Recovery from the spiked water samples and laboratory control samples

The accuracy of the analytical method was evaluated by analyzing laboratory control sample. The recoveries of metals ( Pb, Cd, Cr(VI)) obtained in the spiked laboratory control samples were 104.0 % , 94.8 % and 88.0 % respectively. Similarly, the recoveries of NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> in the spiked laboratory control sample were 95.0 % and 106.0 % respectively.

### **4.3. Determination of Orthophosphate and nitrate in sampled spring water**

#### **4.3.1 Determination of Orthophosphate**

As indicated in Table 3, orthophosphate level in water samples was in the mean range of 0.01 to 0.10 mg/L, which showed that all spring waters are safe in terms of orthophosphate to use as potable water. ANOVA were considered at  $P > 0.05$  and results depicted no significance difference in the concentrations across the sampled sites. Natural water as a whole, rarely contain more than 0.10 mg/L unless they have passed through soil containing phosphate or have polluted by organic matter<sup>11</sup>. Furthermore, phosphate in igneous rocks as apatite which is changed to calcium phosphate lately, is might be unaffected or not found as much considerable as bring to pollution. Therefore, the represented water samples exposure to organo-phosphates and salts of phosphates as very small as contribute little for contaminations. Similarly, in the sampling areas, risks due to exposure of excessive usage of fertilizers which may add phosphate to water and domestic and industrial sewage effluents which may contain considerable amounts of phosphate and use of phosphate detergents was very little if not all in<sup>81, 82</sup>.

#### **4.3.2 Determination of Nitrate**

The results for the parameter Nitrate which has a mean range 13.28 to 281.11 mg/L. As it is presented in Table 3, spring water samples at SWS-01, SWS-02, SWS-03, SWS-05 and SWS-07 were above the permissible limit set by WHO drinking water standards. There were variations across the stations; however, concentrations of nitrates were not significantly different ( $p > 0.05$ ). For the samples which possess high concentrations, the source of  $\text{NO}_3^-$  in the water could be runoff from fertilizer used; leaching from septic tanks, even the small amounts of nitrogen contained in igneous rock might be provided some nitrate to spring waters in the process of weathering since all the nitrate compounds are readily soluble in water, and any formed in weathering would be found in water<sup>83</sup>.

**Table 3:** The Concentration of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  in spring water sampled from Jimma town;  
May 2014

Sampling Sites	Nitrate (mg/L)	Orthophosphate (mg/L)
	$\bar{X} \pm S$	$\bar{X} \pm S$
SWS 01	57.55±2.21	0.01±0.00
SWS 02	75.26±0.00	0.02±0.01
SWS 03	166.01±4.43	0.04±0.01
SWS 04	35.42±2.20	0.04±0.01
SWS 05	121.70±2.22	0.06±0.01
SWS 06	42.06±4.43	0.10±0.06
SWS 07	281.11±4.43	0.01±0.00
SWS 08	13.28±2.21	0.08±0.01
MDL	0.01	0.01
% Recovery	95%	106%
% RSD	10.34	6.45

SWS- Spring water sample

## **4.4 Determination of some heavy metals (Pb, Cd, and Cr (VI))in sampled spring water**

### **4.4.1 Determination of Cadmium and Lead**

As it is presented in Table 4, Cadmium was observed to have above the permissible limit set by WHO drinking water standards at SWS-03, SWS-04, SWS-06, SWS-07 and SWS-08, while having a permissible level within the WHO guideline in the rest of the sampling springs. Also lead was observed to show values above the permissible limit set by WHO drinking water standards at SWS-01, SWS-04, SWS-05 and SWS-08 while the rest sampling springs were within the standards of WHO. In addition, the variations of Pb and Cd concentration in the drinking water were not significant as ANOVA result indicated ( $p > 0.05$ ). The source of these metals in the spring waters can be resulted from the weathering of rocks. For example, lead found in rocks primarily as the sulfide, galena, and also in the form of oxides and occurs in potassium feldspars as well. It may replace certain ions such as calcium and can constitute an appreciable percentage of aragonite. Likewise, the element cadmium is present in rocks in small quantities with zinc and lead. Such suggestions of different groundwater chemistry are forwarded by various studies<sup>76</sup>.

### **4.4.2 Determination of Cr (VI)**

As it is presented in Table 4, the finding of this research showed us, the level of Cr (VI) is mostly found within the WHO guideline value in most sites of spring waters except SWS-04 which is even very less beyond the guideline of WHO permissible level. This might be resulted in minor amounts of igneous rocks<sup>76</sup>. One way ANOVA suggested there were no significant differences in the levels for this metal concentration ( $p > 0.05$ ). Higher concentrations have been reported in ground water of industrial areas but here are not polluting potentials in the area of sampling, where chromium might have been produced and disposed, risk of contamination became insignificant.

**Table 4:** The Concentration of Pb, Cd and Cr (VI), in spring water sampled from Jimma town, May, 2014

Sampling Sites	Pb (mg/L)	Cd (mg/L)	Cr (VI) (mg/L)
	$\bar{X}\pm S$	$\bar{X}\pm S$	$\bar{X}\pm S$
SWS 01	0.0385±0.0015	0.0015±0.0005	0.0120±0.0040
SWS 02	0.0020±0.0000	0.0025±0.0005	0.0160±0.0000
SWS 03	0.0075±0.0005	0.0210±0.0040	ND*
SWS 04	0.0230±0.0010	0.0035±0.0005	0.0520±0.0120
SWS 05	0.0615±0.0015	0.0020±0.0000	0.0400±0.0240
SWS 06	0.0080±0.0010	0.0235±0.0045	0.0280±0.0120
SWS 07	0.0040±0.0015	0.0075±0.0005	0.0240±0.0160
SWS 08	0.0170±0.0080	0.0080±0.0010	0.0280±0.0120
MDL	0.0020	0.0015	0.0028
% Recovery	104%	94.8%	88%
% RSD	12.6	7.42	9.22

- SWS-spring water sample; ND\*-Not Detected

## **4.5 Physico-chemical parameters results of sampled spring water**

### **4.5.1 Color, Taste and Odor**

The physical quality of water (color and taste) also was considered. Water of poor physical quality does not directly cause disease, but it may be aesthetically unacceptable to consumers, and may force them to use less safe sources. Samples from SWS-05, SWS-06 and SWS-08 sites when viewed, they slightly deviated from the color of pure water which should have been light blue and possess a capacity to transmit light through its depth<sup>51</sup>.

Taste refers to a method of sensory analysis in which samples are taken into the mouth. In its pure form, water is odor-free. All the samples under study were unobjectionable; hence they did not have an unpleasant odor and taste. This aesthetic property may inform all spring water are free from excessive ionic inorganic constituents like manganese, zinc and iron which strongly cause undesirable astringent taste and volatile organic chemicals which might result in danger to the consumer and therefore, spring water under this study are suitable for drinking consumption<sup>62</sup>.

#### 4.5.2 pH, Temperature, Conductivity, Dissolved Oxygen, Turbidity and Total suspended solids

The physicochemical analysis of the sampled spring water which was conducted onsite and laboratory is summarized in Table 5

**Table 5:** Physico-chemical parameter results of sampled spring water, Jimma town, May, 2014

Water sample code	Name of Springs	Parameters						
		pH	T <sup>0</sup> (°C)	Cond. (µScm <sup>-1</sup> )	DO		Turbidity (NTU)	TSS (mg/L)
					mgL <sup>-1</sup>	% of Satu.		
SWS 01	Mentina-Key Meskel	6.48±0.03	22.5±0.50	638.0±1.00	1.09±0.01	15.5±0.10	1.14±0.02	2.80 ± 0.10
SWS 02	Agarober-Key Meskel	6.58±0.17	22.7±0.20	410.0±1.20	2.23±0.04	31.7±0.20	1.31±0.02	0.41 ±0.02
SWS 03	Sarsefer-Minch	6.79±0.03	22.7±0.10	88.5±0.60	3.39±0.01	48.3±0.30	4.75±0.15	0.39 ±0.02
SWS 04	Furustale-Minch	7.09±0.02	21.6±0.30	394.0±7.00	3.85±0.04	53.5±0.40	2.51±0.02	0.39 ±0.04
SWS 05	Seto-Key Meskel	6.48±0.04	23.6±0.50	73.6±0.20	3.06±0.03	44.3±0.60	27.7±0.20	0.41±0.01
SWS 06	Aba Arebu	6.57±0.03	22.9±0.30	57.8±0.10	3.27±0.03	46.8±0.30	23.6±0.20	0.38 ±0.01
SWS 07	Tulema	6.49±0.03	23.4±0.40	148.5±0.50	1.38±0.02	19.9±0.20	1.37±0.07	0.42 ±0.04
SWS 08	Motor Buwanbuwa	8.30±0.20	21.9±0.40	85.1±0.45	6.70±0.20	95.0±2.50	7.86±0.01	0.41 ±0.02

SWS-Spring water sample



As it is presented in Table 5, in terms of pH and temperature, all sampled springs were within the permissible limit set by WHO drinking water standards. This could show there was not leaching of dissolved constituents or discharge of acidic wastewater from industries such as metal solutions and organic acids into the groundwater. Likewise, the absence of industries because, they are mainly responsible for temperature and pH changes through the release of heat and chemical loaded effluents into ground water<sup>59</sup>. Similarly, one way ANOVA for both pH and temperature indicated that there was no statistical ( $P > 0.05$ ) significance difference in the samples mean values.

As it is presented in Table-5, the mean variations dissolved oxygen was 1.09 to 6.7 mg/L. DO at sampling site of SWS-08 was relatively highest and it is above the permissible limit. This might be because of relatively lower temperature of the water. Thus, as temperature increases, the amount of dissolved oxygen decreases. As it is indicated in Table 6, other samples reading depicted though at the limiting range of WHO which allows them to use as drinkable water, this could be groundwater, in general, will have low dissolved oxygen content where there is a lack of direct contact with air or where the existing oxygen has been utilized in chemical and microbiological processes. The results of ANOVA for the level of DO also revealed no significance ( $p > 0.05$ ) in the variations<sup>60</sup>.

As it is presented in Table 5, TSS was possessed very small in all sampling sites. All analysis in the protected springs magnified suspended solids were not the cause of problem for the water to use as drinking consumption. This would be the result of the minimum exposure of erosion from urban runoff , agricultural land, industrial wastes, bank erosion, algae growth or wastewater discharges<sup>54</sup>. One way ANOVA for TSS indicated that there was not significance ( $P > 0.05$ ) significance difference in the samples mean values.

Conductivity of water is related to the type and concentration of ions dissolved in the water along with the temperature. As indicated in Table 5, Electrical Conductivity (EC) for sites SWS-01, SWS-02 and SWS-04 were highest; likewise, as it is presented in Table 6, they were above the requirement of WHO permissible limit. This could be due to ionic composition of water; which might be because of Salts of chlorides and sodium most commonly affect groundwater Electrical Conductivity<sup>60</sup>.

As indicated in Table 5, turbidity measured from the water samples had a mean range 1.14 to 27.7 NTU. Furthermore, the results was subjected to 1-way Analysis of variance (ANOVA), and indicated that there was no statistically ( $P > 0.05$ ) significance difference in terms of turbidity. As it is presented in Table 6, the turbidity of spring water sample of SWS-05, SWS-06 and SWS-08 were above permissible limit set by WHO drinking water standards. This could be caused by concentration of suspended matter or is formed by the presence of un-dissolved matter in water<sup>27</sup>.

#### **4.6 Comparison of results with Guideline values for evaluation of their health effect**

The guideline values for the metals and physicochemical parameters in spring water samples recommended by different organizations and countries is presented in Table 6; <sup>47, 69, 84-87</sup>. These heavy metals, physicochemical parameters play their part chemically as well as biologically in organisms and environment either positively or negatively. As the result, these guideline values were required to compare the impacts of their concentration with regard to toxicity and health effect.

**Table 6:** Drinking water contaminants and maximum limit set by different National and International organizations

Organi.	pH	Turb. (NTU)	EC ( $\mu$ S/cm)	TSS ( mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	PO <sub>4</sub> <sup>3-</sup> (mg/L)	Pb (mg/L)	Cd (mg/L)	Cr(VI) (mg/L)	Reference
WHO	6.50-8.50	<5.00	250.00	NM*	50.00	NM*	0.01	0.003	0.05	47,69,84,86
USEPA	6.50-8.50	0.50-1.00	NM*	NM*	10.00	NM*	0.015	0.005	0.10	69
EU	6.50-8.50	NM*	77	25	50.00	5	0.05	0.005	0.05	87
This study	6.48-8.30	1.14-27.7	73.6-638	0.385-2.8	13.28-281.11	0.01-0.10	0.002-0.0615	0.0015-0.0235	Nil-0.052	

NM\*-Not mentioned

## **5. CONCLUSION AND RECOMMENDATION**

### **5.1 Conclusion**

The study assessed the concentration of some of physico-chemical parameters and the level of some heavy metals of the protected spring water samples found in Jimma town. Accordingly, the pH and phosphate level of all sampled spring water was within the permissible range of WHO guideline. Likewise, the level of Cr (VI) of all sampled spring water was within the permissible range of USEPA. However, the rest parameters which was assessed (turbidity, electrical conductivity, total suspended solids, nitrate, lead and cadmium were partly within the permissible range and partly not. For example, among the study sites, 50 % of sampled spring water nitrate concentrations were found to be above the recommended set by WHO guideline. In terms of conductivity and turbidity, some of the protected spring waters measured values were above the standard and this prohibit to use the water for drinking consumption, which might cause health problem.

As it is presented in Table 4, Cadmium showed a higher level beyond the WHO guideline in most of sampled springs (SWS-03,SWS-04, SWS-06, SWS-07and SWS-08) and about 50 % of sampled spring water has lead concentration, which is above the WHO guideline. Therefore; even though, all of the sampled spring waters for this study were protected; they need continuous monitoring and solutions for the parameters which are above the recommended values of EU, USEPA and WHO.

### **5.2 Recommendation**

- Awareness creation to the surrounding community, on the management of the source of inorganic and organic pollutants of spring water of the town has to be given regularly.
- Based on the results of the study, it is strongly suggested that the chemistry of spring water is largely influenced by the specific geologic settings of the area. Therefore; governmental and nongovernmental organizations have to work on sustainable preservation of the spring water of Jimma town from deterioration.

- Further studies are important to assess the level of other ionic species (cations and anions) which will be the cause for high conductivity of spring water.
- The spring water sources in Jimma town should be routinely monitored for physico-chemical and heavy metal analysis to ascertain its suitability for drinking and other purposes.

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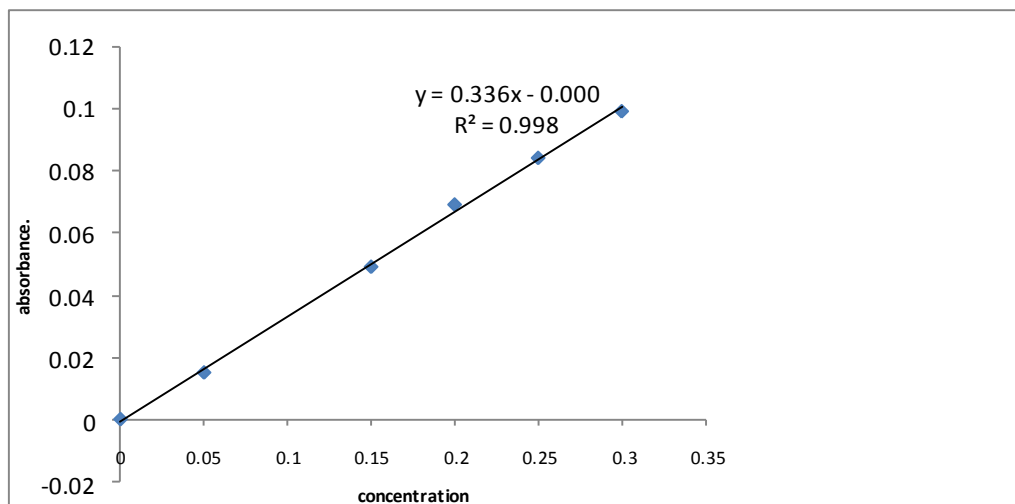
## APPENDICES

**JIMMA UNIVERSITY**  
**SCHOOL OF GRADUATE STUDIES**  
**DEPARTMENT OF CHEMISTRY**

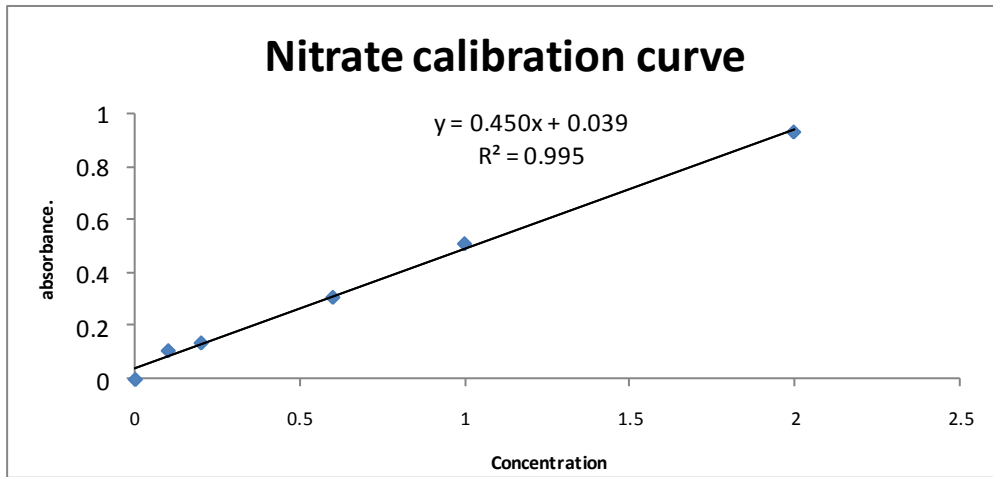
**PHYSICO-CHEMICAL ANALYSIS AND DETERMINATION OF THE LEVEL OF  
SOME SELECTED HEAVY METALS IN SPRING WATER OF JIMMA TOWN**

### APPENDICE I. calibration curve readings

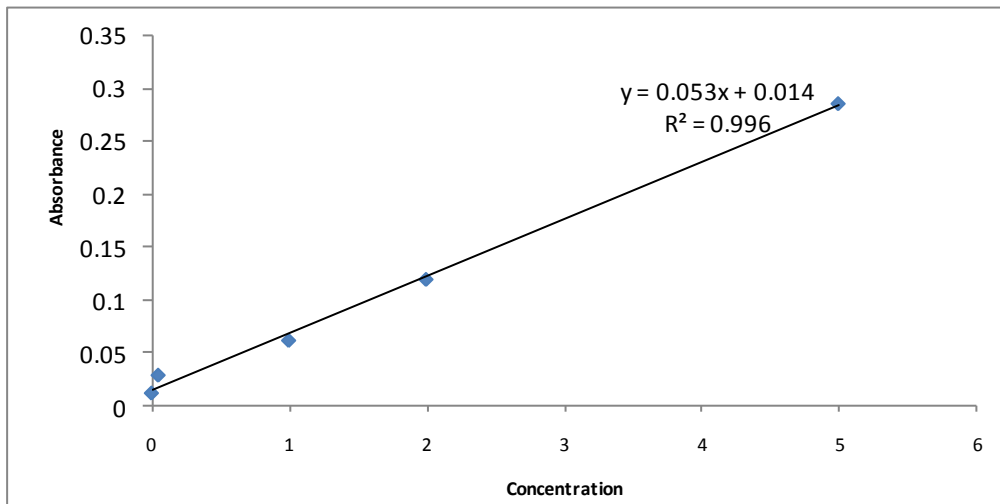
#### 1. Calibration curve reading for determination of Orthophosphate



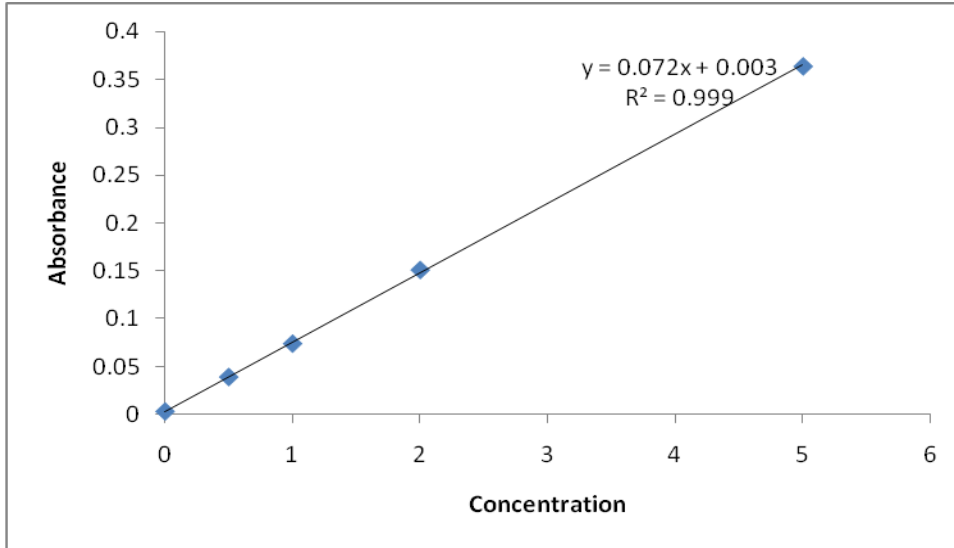
## 2. Calibration curve reading for determination of Nitrate



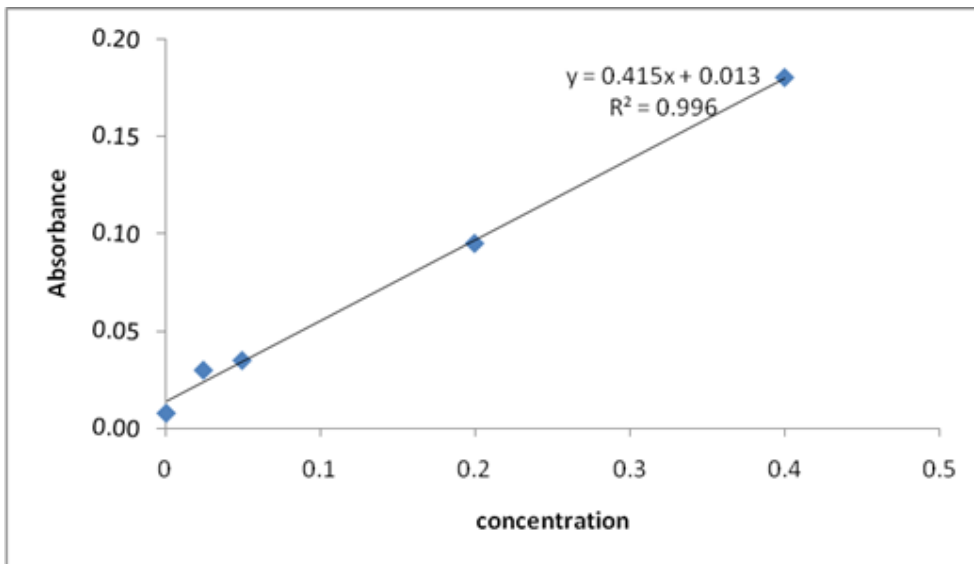
## 3. Calibration curve reading for determination of Lead



#### 4. Calibration curve reading for determination of Cadmium



#### 5. Calibration curve reading for determination of Cr(VI)



## APPENDICE II. ANOVA Results

### 1. Orthophosphate

Anova: Single Factor

#### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
0.01	7	0.37	0.052857	0.000724
0.01	7	0.42	0.06	0.004567

#### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.000179	1	0.000179	0.067507	0.799406	4.747225
Within Groups	0.031743	12	0.002645			
Total	0.031921	13				

### 2. Nitrate

Anova: Single Factor

#### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	779.15	97.39375	7580.755
Column 2	8	805.72	100.715	8175.202

#### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	44.12281	1	44.12281	0.005601	0.941402	4.60011
Within Groups	110291.7	14	7877.979			
Total	110335.8	15				



### 3. Lead

Anova: Single Factor

#### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	0.174	0.02175	0.00042
Column 2	8	0.149	0.018625	0.000444

#### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	3.91E-05	1	3.91E-05	0.090462	0.768011	4.60011
Within Groups	0.006045	14	0.000432			
Total	0.006084	15				

### 4. Cadmium

Anova: Single Factor

#### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	0.061	0.007625	4.83E-05
Column 2	8	0.078	0.00975	0.000113

#### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	1.81E-05	1	1.81E-05	0.224304	0.64308	4.60011
Within Groups	0.001127	14	8.05E-05			
Total	0.001145	15				

## 5. Cr(VI)

Anova: Single Factor

### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	0.184	0.023	0.000227
Column 2	8	0.216	0.027	0.000657

### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	6.4E-05	1	6.4E-05	0.144703	0.709359	4.60011
Within Groups	0.006192	14	0.000442			
Total	0.006256	15				

## 6. Conductivity

Anova: Single Factor

### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	1913.3	239.1625	47566.39
Column 2	8	1877.8	234.725	45944.92

### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	78.76563	1	78.76563	0.001685	0.96784	4.60011
Within Groups	654579.2	14	46755.65			
Total	654657.9	15				

## 7. Dissolved Oxygen (DO)

Anova: Single Factor

### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	25.21	3.15125	3.301327
Column 2	8	24.73	3.09125	2.820755

### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.0144	1	0.0144	0.004704	0.946288	4.60011
Within Groups	42.85458	14	3.061041			
Total	42.86898	15				

## 8. pH

Anova: Single Factor

### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	54.41	6.80125	0.326384
Column 2	8	55.15	6.89375	0.466684

### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.034225	1	0.034225	0.08631	0.773232	4.60011
Within Groups	5.551475	14	0.396534			
Total	5.5857	15				

## 9. TSS

Anova: Single Factor

### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	5.46	0.6825	0.665479
Column 2	8	5.73	0.71625	0.778884

### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.004556	1	0.004556	0.006309	0.937815	4.60011
Within Groups	10.11054	14	0.722181			
Total	10.11509	15				

## 10. Temperature

Anova: Single Factor

### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	181.2	22.65	0.385714
Column 2	8	181.4	22.675	0.833571

### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.0025	1	0.0025	0.004101	0.949846	4.60011
Within Groups	8.535	14	0.609643			
Total	8.5375	15				

## 11. Turbidity

Anova: Single Factor

### SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	8	70.33	8.79125	114.9164
Column 2	8	70.15	8.76875	114.5652

### ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.002025	1	0.002025	1.76E-05	0.996707	4.60011
Within Groups	1606.371	14	114.7408			
Total	1606.373	15				