ADDIS ABABA UNIVERSITY

GRADUATE PROGRAM

Determination of common ions and heavy metals in bottled waters consumed in Ethiopia

By

Mulugeta Assefa

July 2008

Determination of common ions and heavy metals in bottled waters consumed in Ethiopia

GRADUATE PROJECT

(Chem. 774)

SUBMITTED TO:

DEPARTMENT OF CHEMISTREY

ADDIS ABABA UNIVERSITY

In partial fulfillment of requirements for the Degree of

Master of Science in Chemistry

By

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Dedication

To my mother, Aselefech Tefera

Acknowledgements

I am most grateful to my advisors Prof. B. S. Chandravanshi and Dr. Mesfin Redi for their ideas, guidance, comments, criticizing and encouragement to accomplish this work. I thank the Addis Ababa University for allowing me to use the facilities at the university.

Many thanks go to my mother, brother and sister for their material support and moral encouragement in finalizing this project work. I would like to thank my friends Muluberhan, Tegenu, Dereje and Abdulahi for their friendly co-operation and support in various ways.

I am thankful to W/t Amakelech Belete for her technical support during sample analysis. Finally, I would like thank to Oromia Education Bureau allowing me to continue my education and providing sponsorship.

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Lists of Acronyms and Abbreviations

ADWG	Australian Drinking Water Guidelines
ANOVA	Analysis of Variance
BDL	Below the Detection Limit
CAC	Codex Alimentarius Commission
EC	Electrical Conductivity
EU	European Union
FAAS	Flame Atomic Absorption spectrometer
FAO	Food and Agriculture Organization
IC	Ion Chromatography
IDL	Instrument Detection Limit
LOD	Limit of Detection
TDS	Total Dissolved Solid
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
%RSD	Percentage Relative Standard Deviation

Determination of common ions and heavy metals in bottled waters consumed in Ethiopia

By Mulugeta Assefa
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Abstract

Concentration of six trace elements, nine major ions and two physical parameters in six different brands of bottled water obtained from Ethiopia were investigated. For comparison purpose, sample of tap water from Addis Ababa was also analysed. Cd, Cu, Cr, Fe, Pb, Zn, Na, K, Mg and Ca contents of the drinking water samples were determined by FAAS. Concentrations of F^-, Cl^-, NO_3^-, $SO_4^{2-}$and PO_4^{3-} were determined by IC. The data showed the variation of the investigated parameters in water samples as follows: Fe 0.035-0.086 mg/L, Zn 0.088-0.334 mg/L, Na 2.77-48.03 mg/L, K 1.19-4.40 mg/L, Mg 1.30-3.42 mg/L, Ca 1.63-11.59 mg/L, F^- < 0.20-0.92 mg/L, Cl^- 4.84-12.38 mg/L , NO_3^- < 0.42-8.38 mg/L, SO_4^{2-} < 0.36-10.26 mg/L pH 7.35-8.34 and EC 119.7-579.3 µS/cm. Cd, Cu, Cr, Pb and PO_4^{3-} concentrations in all the drinking water samples were below the detection limit. Concentration levels of all the analysed trace metals and common ions investigated in all examined water samples were below the maximum contaminant level prescribed by WHO regulations. Some of the physical parameters, pH and electrical conductivity were determined. pH in all the samples was with in the permissible limit of WHO drinking water quality guidelines.

Key Words: FAAS, IC, Bottled Water, Metal, Common Anions, Physical Parameters

1. INTRODUCTION

After oxygen, water is the most vital substance for maintaining life and one of the most important resources worldwide. It is consumed by billions of people all over the world daily and used for agricultural and industrial production [1]. Water is the most commonly used chemical solvent in our everyday lives. But, the water that we use or drink is in fact not just a composition of hydrogen and oxygen (H_2O) but rather a large list of other elements that can be found in the water. Thus, the water that we drink may seem clean, but it is not pure. Therefore, water can have many differences depending on the amount of each elements and microorganisms in it [2]. In the past, epidemics of waterborne diseases resulted from pathogenic microorganisms in water supplies. For the most part, a greater concern with water safety now is the potential presence of chemical pollutants. These may include organic chemicals, inorganic chemicals and heavy metals from industrial, urban runoff, and agricultural sources [3].

Water is an essential component for life and its analysis for chemical properties including heavy metal contents are very important for public health studies [4]. Heavy metals occur in nature and most of them are advantageous to humans because of their vast usages in different industries, agriculture, and medicine. However, they may pose health hazards to the public because of their presence in air, water and food [5]. Furthermore water pollution by heavy metal is mainly caused by point source emissions from mining activities and a wide variety of industries [5, 6]. Heavy metals include essential elements like such as Co, Cr, Cu, Fe, Mn, Mo, Se and Zn as well as toxic metals like Ag, Al, As, Cd, Pb and Ni. Certain essential trace elements can be toxic when concentrations are raised above specific cut-off levels [7] and the elements which are toxic when present in higher concentrations could be very useful in small amounts [8].

A number of chemical contaminants have been shown to cause adverse health effects in humans as a consequence of prolonged exposure through drinking water. Exposure to high levels of fluoride, which occurs naturally, can lead to mottling of teeth and, in severe cases, crippling skeletal fluorosis. Nitrate may arise from the excessive application of fertilizers or from leaching of wastewater or other organic wastes into surface water and groundwater. Particularly in areas with aggressive or acidic waters, the use of lead pipes and fittings or solder can result in elevated lead levels in drinking water, which cause adverse neurological effects. There are few chemicals for which the contribution from drinking water to overall intake is an important factor in preventing disease. One example is the effect of fluoride in drinking water in increasing prevention against dental caries [9].

Drinking water may be contaminated by a range of chemical, microbial and physical hazards that could pose risks to health if they are present at high levels. Because of the large number of possible hazards in drinking water, the development of standards for drinking water requires significant resources and expertise, which many countries are unable to afford. Fortunately, guidance is available at the international level. International trade in bottled water has increased in recent years, both in quantity and diversity. Aside from water shortages, real and perceived needs to improve health also have contributed to a growing trade in bottled water. Increasingly it has been recognized that traditional suppliers of drinking water such as public and private waterworks may not always be able to guarantee the microbiological, chemical and physical safety of their product to the extent previously thought possible [10].

The World Health Organization (WHO) publishes *Guidelines for Drinking-water Quality* which many countries use as the basis to establish their own national standards. The *Guidelines* represent a scientific assessment of the risks to health from biological and chemical constituents of drinking water and of the effectiveness of associated control measures. WHO recommends that social, economic and environmental factors be taken into account through a risk-benefit approach when adapting the *Guideline* values to national standards. As the WHO *Guidelines for Drinking-water Quality* are meant to be the scientific point of departure for standards development, including bottled water; actual standards will sometimes vary from the *Guidelines* [11].

1.1 Literature Review

1.1.1 Drinking Water

Drinking water is defined as water intended primarily for human consumption, either directly, as supplied from the tap, or indirectly, in beverages, ice or foods prepared with water. Drinking water is also used for other domestic purposes such as bathing and showering. There is clear evidence that the common adoption of chlorination of drinking water supplies in the 20th century was responsible for a substantial decrease in infectious diseases. Water quality testing has limitations and there are many possibilities for contamination of water in reticulation systems after treatment. Drinking water does not need to be absolutely pure to be safe. Because water is such good solvent, pure water containing nothing else is almost impossible to attain. What is required is that drinking water should be safe to drink for people in most stages of normal life, including children over six months of age and the very old. It should contain no harmful concentrations of chemicals or pathogenic microorganisms, and ideally it should be aesthetically pleasing in regard to appearance, taste and odor [12].

1.1.2 Characteristics of Drinking Water Quality

The safety of water, in public health terms, is determined by its microbiological, physical, chemical and radiological quality [9].

Microbiological Quality: The principal risk to human health from drinking water is the presence of pathogenic microorganisms. The most common and widespread health risk associated with drinking water is contamination, either directly or indirectly, by human or animal excreta and the microorganisms contained in faeces. Drinking such contaminated water or using it in food preparation may cause new cases of infection. The degree of risk is related to the level of disease in the human or animal community at that time. Those at greatest risk of infection are infants and young children, people whose immune system is suppressed, the sick, and the elderly. Pathogenic organisms of concern include bacteria, viruses and protozoa; the diseases they cause vary in severity from mild gastroenteritis to severe and sometimes fatal diarrhea, dysentery, hepatitis, cholera or typhoid fever [13].

Physical Quality: Physical characteristics are most often used by consumers to judge water quality [14]. The measurable characteristics that determine these largely subjective qualities are: true colour, turbidity, hardness, total dissolved solids (TDS), pH, temperature, dissolved oxygen, taste and odour [12]. Colour and turbidity influence the appearance of water. Taste can be influenced by temperature, TDS, and pH. The 'feel' of water can be affected by pH, temperature, and hardness. Rates of corrosion and encrustation of pipes and fittings are affected by pH, temperature, hardness, TDS and dissolved oxygen [13]. Water should be free of tastes and odours that would be objectionable to the majority of consumers. In assessing the quality of drinking water, consumers rely principally upon their senses. Microbial, chemical and physical water constituents may affect the appearance, odour or taste of the water and the consumer will evaluate the quality and acceptability of the water on the basis of these criteria. Although these substances may have no direct health effects, water that is highly turbid, is highly coloured or has an objectionable taste or odour may be regarded by consumers as unsafe and may be rejected [9].

Chemical Quality: There are few chemical constituents of water that can lead to health problems resulting from a single exposure, except through massive accidental contaminations of a drinking water supply. Moreover, experience shows that in many, but not all, such incidents, the water becomes undrinkable owing to unacceptable taste, odours and appearance. In situations where short-term exposure is not likely to lead to health impairment, it is often most effective to concentrate the available resources for remedial action on finding and eliminating the source of contamination, rather than on installing expensive drinking water treatment for the removal of the chemical constituent [9]. A number of chemicals, both organic and inorganic, including some pesticides, are of concern in drinking water from the health perspective because they are toxic to humans or are suspected of causing cancer; some can also affect the aesthetic quality of water [13].

a. Inorganic Chemicals: Inorganic chemicals in drinking water usually occur as dissolved salts such as carbonates and chlorides, attached to suspended material such as clay particles, or as complexes with naturally occurring organic compounds [13].

b. Organic Compounds: Organic compounds are usually present in drinking water in very low concentrations; they may occur either naturally or as a result of human activities. Contamination of drinking water by pesticides may occur occasionally as a result of accidental spills, misadventure, or emergency use of pesticides [13].

Radiological Quality: Radioactive materials occur naturally in the environment (e.g. uranium, thorium and potassium). Some radioactive compounds arise from human activities (e.g. from medical or industrial uses of radioactivity) and some natural sources of radiation are concentrated by mining and other industrial activities. By far the largest proportion of human exposure to radiation comes from natural sources and from external sources of radiation, including cosmic radiation, or from ingestion or inhalation of radioactive materials. A very low proportion of the total human exposure comes from drinking water [13]. Formal guideline values are not set for individual radionuclides in drinking water. According to Kovács *et al.*, some kinds of mineral waters contain naturally occurring radionuclides in higher concentration than the usual drinking (tap) water [15].

1.1.3 Drinking Water Contaminants

Chemical contaminants in drinking water may be categorized in various ways; however, the most appropriate is to consider the primary source of the contaminant, i.e. to group chemicals according to where control may be effectively exercised. This aids in the development of approaches that are designed to prevent or minimize contamination, rather than those that rely primarily on the measurement of contaminant levels in final waters [9]. The determination of trace heavy metal is becoming increasingly important because of the increased interest in environmental samples including water, soil and plant, etc [16].

Once a toxic chemical enters the body its effect is determined by the interplay of absorption, distribution, metabolism and excretion. The nature, number, severity and/or prevalence of specific effects generally increase with increasing dose. Metals in drinking water can cause taste and staining problems. Staining problems are usually associated with iron, copper and manganese. Taste problems are usually due to iron, copper, manganese or zinc. The metals that usually appear at the highest concentrations are iron, copper and zinc. Iron and zinc may arise from iron pipes or galvanised or brass fittings in the distribution system. Copper is more likely to arise from the corrosion of the consumer's own plumbing, although both iron and zinc may also appear in water from the dissolution of materials on the consumer's property [17].

The toxicity of metals is dependant on their solubility and this in turn depends on pH and on the presence of different types of anions and cations. Water pollution has been a subject of active investigation for a long time. Interest in this has grown because of the perceived hazardous effects of trace element [18]. Heavy metals come from local sources mostly industry, agriculture, water incineration, burning of fossil fuels and road traffic [9]. In heavily polluted waters, excessive plant and algal growth can degrade the water quality and are a very visible cause of the taste and odour problem [19]. It is desirable to control the intake of these potentially toxic chemicals from drinking water because the intake from other sources such as milk, food or air may be difficult to avoid. In general, total environmental exposure, food intake, and possible adverse effects from long-term exposure have been taken into consideration in deriving the standard [14].

1.1.4 Health Aspects of Minerals in Drinking Water

All natural water sources contain a variety of chemicals. These consist of those that are naturally occurring and those that arise as a consequence of man's activity. The natural inorganic constituents are minerals that leach from rocks and soil through which the water percolates. The mineral content contributes to the taste of drinking water and some highly mineralized waters are prized for their taste or reputed health-giving properties [20]. Safe drinking water is suitable for all usual domestic purposes, including personal hygiene. A guideline value normally represents the concentration of a constituent that does not result in any significant risk to health over a lifetime of consumption. A number of provisional guideline values have been established based on the practical level of treatment achievability or analytical achievability [9].

1.1.4.1 Heavy Metals

Cadmium: Cadmium metal is used in the steel industry, in plastics and batteries. Cadmium is released to the environment in wastewater, and diffuse pollution is caused by contamination from fertilizers and local air pollution. Contamination in drinking water may also be caused by impurities in the zinc of galvanized pipes and solders and some metal fittings. Food is the main source of daily exposure to cadmium. Smoking is a significant additional source of cadmium exposure [3]. The main critical effects include increased excretion of low-molecular weight proteins in the urine and an increased risk of osteoporosis. Other effects can include osteomalacia (softening of the bones). Epidemiological studies have looked for a connection between lung cancer and workplace cadmium inhalation, but the results have been inconclusive [13]. Population groups at risk include the elderly, people with diabetes, and smokers [21].

Chromium: Chromium is widely distributed in the earth's crust. It can exist in valences of +3 and +6. In general, food appears to be the major source of intake [9]. Trivalent chromium (Cr^{3+}) salts are used in leather tanning, manufacture of catalysts, paint pigments, fungicides, and ceramic and glass manufacture. Hexavelent chromium (Cr^{6+}) occurs infrequently in nature. Its presence in water is generally the result of industrial and domestic chromium waste discharges. Cr^{6+} compounds are used in the metallurgical industry for chrome alloy and chrome metal production, and in the chemical industry as oxidising agents [13]. The absorption of chromium after ingestion is low and depends on the valence state. Cr^{6+} is more readily absorbed from the gastrointestinal tract than Cr^{3+} compounds. It is able to penetrate cell membranes, and within cells it is reduced to Cr^{3+} and forms complexes with proteins and genetic material. Epidemiological studies have found an association between inhalation of Cr^{6+} compounds and lung cancer, especially in humans occupationally exposed during chromate production. There is no evidence that organs other than the lung are affected or that ingestion of Cr^{6+} compounds can cause cancer [13].

Copper: Copper is both an essential nutrient and a drinking water contaminant. It has many commercial uses. It is used to make pipes, valves and fittings and is present in alloys and coatings. Copper sulfate pentahydrate is sometimes added to surface water for the control of algae [9]. Copper is stored in the liver, brain and muscle tissue. High concentrations can also be found in the kidneys, heart and hair. Copper is eliminated from the body mainly in the bile. Copper poisoning has resulted in cirrhosis of the liver and, in extreme cases, death. Other less severe symptoms associated with the consumption of water containing 3-5 mg/L copper are gastrointestinal symptoms such as nausea, abdominal pain and vomiting [13].

Iron: Elemental iron is rarely found in nature, as the iron ions Fe^{2+} and Fe^{3+} readily combine with oxygen and sulfur containing compounds to form oxides, hydroxides, carbonates, and sulfides. Iron oxides are used as pigments in paints and plastics. Other compounds are used as food colours and for the treatment of iron deficiency in humans. Various iron salts are used as coagulants in water treatment. In well-water, iron concentrations below 0.3 mg/L were characterized as unnoticeable, whereas levels of 0.3-3 mg/L were found acceptable [22]. Iron is an essential trace element for humans. Numerous cases of iron poisoning have been reported, mainly among young children who ingest medicinal iron supplements formulated for adults. Physiological regulation of iron absorption confers a high degree of protection against iron toxicity and there are a number of reports of people, particularly adults, taking high doses of iron with no adverse effects [13].

Lead: Lead is used principally in the production of lead-acid batteries, solder and alloys. The organolead compounds tetraethyl and tetramethyl lead have also been used extensively as antiknock and lubricating agents in petrol, although their use for these purposes in many countries is being phased out. Lead is rarely present in tap water as a result of its dissolution from natural sources; rather, its presence is primarily from household plumbing systems containing lead in pipes, solder, fittings or the service connections to homes [9]. Lead is a toxic heavy metal and can affect many organs in the human body [23]. Lead accumulates in the skeleton, and its mobilization from bones during pregnancy and lactation causes exposure to fetuses and breastfed infants. Hence, the lifetime exposure of woman before pregnancy is important [21].

Zinc: Zinc is an essential trace element for the human organism that plays an important role in several biochemical pathways. It is found in virtually all food and potable water in the form of salts or organic complexes [24]. The diet is normally the principal source of zinc. Although levels of zinc in surface water and groundwater normally do not exceed 0.01 and 0.05 mg/L, respectively, concentrations in tap water can be much higher as a result of dissolution of zinc from pipes. Drinking water containing zinc at levels above 3 mg/L may not be acceptable to consumers [9]. Nutritional zinc deficiency results in retarded growth, anorexia, mental lethargy, skin changes and night blindness. Approximately 20-30% of dietary zinc is absorbed by the gastrointestinal tract. Highest concentrations are found in the liver, kidney, bone, retina, prostate and muscle. In humans, consumption of very high amounts of zinc can result in nausea, vomiting, diarrhoea and abdominal cramps. The major effects of long-term exposure to zinc are anaemia and gastric erosion [13].

1.1.4.2 Common Cations

Sodium: Sodium is a component of common salt. It is present in seawater and brackish groundwater. The standard is 200 mg/L [25]. Sodium salts (e.g., sodium chloride) are found in virtually all food and drinking water. It should be noted that some water softeners can add significantly to the sodium content of drinking water [9]. Sodium is essential to human life but there is no agreement on the minimum daily amount needed to maintain health [13]. Sodium is present in all body tissues and fluids and its concentration is maintained by the kidney; increases in the sodium concentration in plasma give rise to the sensation of thirst. Excessive sodium intake, usually via diet, can severely aggravate chronic congestive heart failure. While it is clear that reduced sodium intake can reduce the blood pressure of some individuals with hypertension, it is equally clear that this type of therapy is not effective in all cases. Health authorities are of the opinion, however, that reduced sodium intake is beneficial [13].

Potassium: Potassium is an essential element in humans. It is not commonly found in drinking water at levels that could be a concern to human health. However, the consumption of drinking water treated by water softeners using potassium chloride may significantly increase exposure to potassium. However, increased exposure to potassium could result in significant health effects in people with kidney disease or other conditions, such as heart disease, coronary artery disease, hypertension, diabetes, and who are taking medication that interfere with normal body potassium handling [26].

Calcium: Calcium is a major constituent of various types of rock. It is one of the most common constituents present in natural waters ranging from zero to several hundred milligrams per liter depending on the source and treatment of the water. Calcium is a cause for hardness in water and incrustation in boilers. Calcium is a substantial component of bones and teeth. It plays a role in intracellular information transmission and the coagulability of blood [27].

Magnesium: Magnesium is a common constituent in natural water. Magnesium salts are important contributors to the hardness of water which break down when heated, forming scale in boilers. The magnesium concentration may vary from zero to several hundred milligrams. Chemical softening, reverse osmosis, electro dialysis, or ion exchange reduces the magnesium and associated hardness to acceptable levels. Magnesium plays an important role as a cofactor and activator enzymatic reactions including glycolysis and ATP metabolism [27].

1.1.4.3 Common Anions

Fluoride: The most important source of fluoride in drinking water is naturally occurring. Inorganic fluoride-containing minerals are used widely in industry for a wide range of purposes, including aluminum production. Daily exposure to fluoride depends mainly on the geographical area. In most circumstances, food seems to be the primary source of fluoride intake, with lesser contributions from drinking water and from toothpaste. In areas with relatively high concentrations, particularly in groundwater, drinking water becomes increasingly important as a source of fluoride [9]. Many health authorities around the world recommend de-fluoridation of public water supplies as an important public health measure. Concentrations above 1.5 mg/L may disturb tooth mineralisation in children up to about 6 to 8 years, leading to dental fluorosis, a mottling of the teeth which can occasionally occur to an unsightly degree. Skeletal fluorosis, characterised by hypermineralisation and thus brittle bones, has occurred in association with high fluoride concentrations in drinking water, and also with occupational exposure to fluoride containing dust. It generally occurs after prolonged exposure (several years) and is reversible: if the exposure is removed, the fluoride levels in bones gradually decline [13].

Chloride: Chloride is an ‘essential’ mineral for humans and abundant in ionic trace mineral preparations [28]. Chloride in drinking water originates from natural sources. The main source of human exposure to chloride is the addition of salt to food, and the intake from this source is usually greatly in excess of that from drinking water. Excessive chloride concentrations increase rates of corrosion of metals in the distribution system, depending on the alkalinity of the water. This can lead to increased concentrations of metals in the supply. No health-based guideline value is proposed for chloride in drinking water. However, chloride concentrations in excess of about 250 mg/L can give rise to detectable taste in water [9]. Chloride is absorbed almost completely by the gastrointestinal tract. Healthy individuals can tolerate the intake of large quantities of chloride provided there is a corresponding intake of fresh water. Little is known about the prolonged intake of large amounts of chloride by humans. Large salt intake has been reported to increase blood pressure but this is attributed to the sodium content rather than chloride [13].

Nitrate: Nitrate is naturally occurring ion that is part of the nitrogen cycle. It is used mainly in inorganic fertilizers, and sodium nitrite is used as a food preservative, especially in cured meats. The nitrate concentration in ground water and surface water is normally low but can reach high levels as a result of leaching or runoff from agricultural land or contamination from human or animal wastes as a consequence of the oxidation of ammonia and similar sources [9]. The toxicity of nitrate to humans is thought to be solely due to its reduction to nitrite. The major biological effect of nitrite in humans is its involvement in the oxidation of normal haemoglobin to methaemoglobin, which is unable to transport oxygen to the tissues. This condition is called methaemoglobinaemia. Young infants are more susceptible to methaemoglobin formation than older children and adults [13, 19].

Sulfate: Sulfates occur naturally in numerous minerals and are used commercially, principally in the chemical industry. They are discharged into water in industrial wastes and through atmospheric deposition; however, the highest levels usually occur in groundwater and are from natural sources. Sulfate is rapidly absorbed by the gastrointestinal tract but a number of factors, such as the accompanying cation, can influence the rate of absorption. Low doses are probably absorbed more effectively than high doses. Sulfate is one of the least toxic anions. However, the presence of high concentration in the drinking water may lead to dehydration, stomach complaints and diarrhoea [29]. Ingestion of high doses can result in catharsis (loosening of the bowels) with dehydration as a possible side effect. Sulfate can interfere with disinfection efficiency by scavenging residual chlorine. It can also increase corrosion of mild steel pipes [13].

Phosphate: Phosphorus is one of the key elements necessary for growth of plants and animals. Phosphates PO_4^{3-} are formed from this element. Phosphates can be produced and may occur in water in two forms. Phosphorus in freshwater and marine systems exists in either a particulate phase or a dissolved phase. Phosphates are not toxic to people or animals unless they are present in very high levels. Digestive problems could occur from extremely high levels of phosphate. Phosphate itself does not have notable adverse health effects [30].

1.1.4.4 pH and Electrical Conductivity

pH: No health-based guideline value is proposed for pH. Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters [9]. It is a measure of acid-base equilibrium in natural water. The direct effects of exposure of humans and animals to extreme pH values (below 4 or above 10) for extended periods of time may result in irritation to the eye, skin and mucous membranes. In sensitive individuals gastrointestinal irritation may also occur, however, occasional pH changes may not have any direct impact on water consumers [19]. One of the major objectives in controlling pH is to minimize corrosion and encrustation in pipes and fittings. Corrosion can be reduced by the formation of a protective layer of calcium carbonate on the inside of the pipe or fitting, and the formation of this layer is affected by pH, temperature, the availability of calcium (hardness) and carbon dioxide [13].

Electrical Conductivity (EC): This a measure of the general amounts of mineral salts dissolved in water**.** The electrical conductivity is the important characteristic parameters for distinguishing differences among mineral waters [29]. It is also a non-specific measure of the amount of natural dissolved inorganic substances in source waters.

1.1.5 Bottled Waters

Bottled water can come from wells, springs, artesian wells, or the municipal water supply [31]. Bottled waters are widely available in both industrialized and developing countries. Consumers may have various reasons for purchasing packaged drinking water, such as taste, convenience or fashion; for many consumers, however, safety and potential health benefits are important considerations. Water is packaged for consumption in a range of vessels, including cans, laminated boxes and plastic bags, and as ice prepared for consumption. However, it is most commonly prepared in glass or plastic bottles. The biggest consumers of bottled waters in the world are western countries. Per year consumption in Germany, France, Switzerland, Italy and Belgium is over 100 L per capita. Production and consumption of bottled waters are rapidly increasing in many European countries, becoming an important component of their economies [32]. Mineral water has been gaining in popularity over the last decades. The increasing number of mineral waters for sale at supermarkets raises more questions about the differences between these mineral waters, both when compared to each other and when compared to tap water. Like any other product for human consumption mineral water needs to be periodically tested for microbiological and chemical composition [33].

However, some substances may prove to be more difficult to manage in bottled water than in tap water. Other problems may arise because bottled water is stored for longer periods and at higher temperatures than water distributed in piped distribution systems or because containers and bottles are reused without adequate cleaning or disinfection. Control of materials used in containers and closures for bottled water is, therefore, of special concern. Some microorganisms that are normally of little or no public health significance may grow to higher levels in bottled water. This growth appears to occur less frequently in gasified water and in water bottled in glass containers than in still water and water bottled in plastic containers.

The *Guidelines for Drinking-water Quality* provide a basis for derivation of standards for all packaged waters. As with other sources of drinking water, safety is pursued through a combination of safety management and end product quality standards and testing. The international framework for packaged water regulation is provided by the Codex Alimentarius Commission (CAC) of WHO and the FAO. CAC has developed a *Standard for Natural Mineral Waters* and an associated Code of Practice. The *Standard* describes the product and its compositional and quality factors, including limits for certain chemicals, hygiene, packaging and labeling. The CAC has also developed a *Standard for Bottled/Packaged Waters* to cover packaged drinking water other than natural mineral waters. Both relevant CAC standards refer directly to these Guidelines [9].

It should be noted that neither the CAC nor WHO offer certification of any bottled or mineral water products. In this regard, WHO does not permit its name or emblem to be used in connection with any commercial purposes. While many countries have national standards for bottled waters and some have national certification schemes, no universally accepted international certification scheme now exists. Persons seeking information on bottled water certification should approach the national authorities in the country concerned. Codex Alimentarius distinguishes natural mineral water from ordinary drinking water because it is characterized by its content of certain mineral salts and their relative proportions and the presence of trace elements or of other constituents and it is packaged close to the point of emergence of the source with particular hygienic precautions [10, 11].

1.2 Bottled Water in Ethiopia

Bottled waters market is increasing and more brands of bottled waters appear in Addis Ababa shopping centers. These bottled waters are consumed by a number of people. These are Ambo natural mineral water, Highland spring water, Aquaddis spring water, Abyssinia spring water, Aqua Safe natural spring water, Crystal mineral water, Kool natural mineral water, Oasis spring natural water and Real spring natural water. The chemical composition of the first three brands (Ambo, Highland and Aquaddis) was studied by Seda 2007 [34]. In this study, Abyssinia, Aqua Safe, Crystal, Kool, Oasis and Real Springs brands are included. All the brands provided chemical analysis data except Crystal. The most frequently listed parameters on the label are Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, pH and TDS, which were found on five labels. Four brands listed HCO_3^{-}. Other listed parameters were NO_3^{-} and Fe (two each), Al^{3+} and F^{-} (one each) and NO_2^{-} (one brand). Among six brands, Crystal was the only packaged in glass while others were packaged in plastic bottles. In this paper, bottled water has been used to denote natural mineral water, natural spring water and fortified mineral water. More over bottle labels were used as basic information on six brands. The brand, description, package and manufacturer of bottled water selected in the present study are given in Table 1.

Table 1. Brand, description and manufacturer of bottled water

Brand	Description	Manufacturer
Abyssinia Springs	Natural spring water	Great Abyssinia PLC
Aqua Safe	Pure natural spring water	Debre Birhan natural spring water PLC
Crystal	Fortified mineral water	Coca-Cola company
Kool	Natural mineral water	MOHA drinks industry SC
Oasis Spring	Pure natural water	Pacific industries
Real Springs	Purified natural spring water	TGMD trade work PLC

In Ethiopia, there are no regulations governing the mineral water bottled market. Anyone can go to any water source, bottle the water, call it 'Natural Spring Water' and sell it in shops without doing any analysis at all. Therefore it is important to determine and compare the content of bottled waters consumed in Ethiopia with that of worldwide standards in general and the ions listed on labels of bottled mineral water in particular. This research was carried out to provide the concentration of ten metals and five anions in six brands of bottled water currently present on the Ethiopia market. For comparison, tap water was analyzed for the same metals and anions.

1.3 Objective of the Research

1.3.1 General Objective

The main objective of this project is to determine metals and common anions in bottled mineral water consumed in Ethiopia.

1.3.2 Specific Objective

The specific objective of this project includes:

1. To determine metals (Cd, Cr, Cu, Fe, Pb, Zn, Na, K, Ca, Mg) and anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) in the bottled water samples (Abyssinia Springs, Aqua Safe, Crystal, Kool, Oasis Spring and Real Springs Natural Mineral Waters).
2. To determine metals and anions in the Addis Ababa municipal tap water.
3. To compare the levels of heavy metals and anions in the municipal tap water and the bottled waters.
4. To compare the levels of metals and anions in the bottled waters consumed in Ethiopia with that in the other countries in world.

5. To compare the levels of metals and anions in the municipal tap water and the bottled waters consumed in Ethiopia with the World Health Organization and other world water bodies guidelines for drinking waters.

2. EXPERIMENTAL

2.1 Instrumentation and Apparatus

For the analysis of bottled water and tap water samples, two methods were selected. For the determination of metals (Cd, Cr, Cu, Fe, Pb, Zn, Na, K, Ca, Mg); flame atomic absorption spectroscopy (FAAS) was selected. And for the analysis of common anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}); ion chromatography (IC) was used. Therefore the apparatus used in each of the two methods are discussed separately in the following section.

2.1.1 FAAS Apparatus

The concentrations of Cd, Cr, Cu, Fe, Pb, Zn, Na, K, Ca and Mg were determined by FAAS, BUCK SCIENTIFIC MODEL 210VGP (East Norwalk, USA) Atomic Absorption Spectroscopy equipped with deuterium ark back ground correctors, cathode lamps for each respective element, and air-acetylene flame.

2.1.2 IC Apparatus

For the analysis of common anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}); ion chromatography was carried out using a Dionex gradient HPLC system DX-600 (Dionex USA) equipped with an ED50 Electrochemical detector, Dionex LC25 chromatography oven, Electric Rheodyne injection valve, heating range of 30 to 45 ^{0}C Built-in electrochemical cell. And Autosampler (Dionex AS50) was used for sample preparation and temperature control. Isocratic separation of anions was performed on IonpacAS17 anion exchange column-Atlas electrolytic suppressor and IonAS17 analytical column (4 x 250 mm)-0.55682. IonpacAG17 guard column (4 x 50 mm)-055684 was also used in connection with the analytical column for anions. Dionex GS50 Gradient pump and EG40 eluent generator containing cartridge-058900 for generating eluent to the separator system were used for the analysis of anions. The data acquisition and instrument setting were performed by PeakNet6 software. PeakNet6 is a chromatography system for data acquisition, processing, and reporting. It provides real-time bidirectional control via DX-LAN of GS50 pumps; ED50 detector; AS50 Autosampler; and EG40 Eluent Generator.

2.2 Chemicals and Reagents

For the analysis of metals (Cd, Cr, Cu, Fe, Pb, Zn, Na, K, Ca, Mg), HNO_3 (69-72%, Spectrosol, BDH, England) was used for acidifying the water samples, deionized water was used for washing apparatus and for dilutions of standard solutions. Stock solutions of metals (Cd, Cr, Cu, Fe, Pb, Zn, Na, K, Ca, Mg) 1000 mg/L (calibration standard Buck Scientific, USA, prepared as nitrate for each element in 2% HNO_3 were used for the preparation of calibration curves for the determination of metals in the bottled water samples.

In the analysis of common anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) by ion chromatography, H_2SO_4 (20 mM) (BDH limited pool, England) was used for eluting the cations while KOH (20 mM) (BDH limited pool, England) was used for eluting the anions. Composite standard solution of anions that contains (20 mg/L fluoride, 100 mg/L chloride, 100 mg/L nitrate, 100 mg/L sulfate, 200 mg/L phosphate) was used for the analysis of anions which was prepared by the Dionex company (USA) from sodium salts of the anions in ultra pure deionized water (99.9% water). These composite primary standards were used for preparing working standard solutions by diluting of the primary standard solution in deionized water. Composite working standards at lower analyte concentrations were prepared from composite primary standard anions measured in 100 mL volumetric flasks. The working standard solution of anions containing 2 mg/L fluoride, 10 mg/L chloride, 10 mg/L sulfate, 10 mg/L nitrate, and 20 mg/L phosphate were used for single point calibration standards. This single point calibration standard solution was used for correlating the retention time of the analyte in the samples to that of the standard for qualitative determination of the analyte in that given sample and also to relate the peak area of the analyte to that of the standard for quantitative determination.

2.3 Procedures

2.3.1 Sample collection and preparation

Six brands of bottled minerals water samples: Abyssinia Springs, Aqua Safe, Crystal, Kool, Oasis Spring, Real Springs were purchased from local shops and local super markets around Arat Kilo, Addis Ababa. Five bottles were purchased for each brand for the analysis of metals (Cd, Cr, Cu, Fe, Pb, Zn, Na, K, Ca, Mg) and common anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}). One of the six brands was packaged in 330 mL glass container (Crystal) but five brands were in plastic container and capacity of 1 L (Aqua Safe and Kool), 1.5 L (Real Springs), 1.8 L (Abyssinia Springs) and 2 L (Oasis Spring).

The bottled water samples were kept sealed and refrigerated at 4 ^{0}C until the time of analysis. Tap water samples were collected from five different locations of Addis Ababa city for comparison purpose. Prior to sampling, the water was flushed for two minutes and the containers were rinsed three times with the water to be sampled. A tap water sample kept in the sealed flask and refrigerated with that of bottled waters at the same temperature until the time of analysis. For the determination of metals (Cd, Cr, Cu, Fe, Pb, Zn, Na, K, Ca, Mg) by FAAS, all samples were filtered using Whatman filter paper to remove the bubbles from the sample and then, the filtrate was acidified with concentrated nitric acid (69-72% HNO_3) by adding 1 mL of the acid into 50 mL of the sample solution. The acidified samples were preserved in the refrigerator for the analysis.

2.3.2 Analytical Procedures for Metal Analysis

The Flame Atomic Absorption Spectrometry (FAAS) is the most often used instrumental techniques for the determination of many elements in different types of natural waters, including rain waters, fresh waters, mineral waters, brines and wastewaters [22]. Atomic absorption spectroscopic standard solutions containing 1000 mg/L were used for preparing intermediate standard solutions (10 mg/L) in 100 mL volumetric flask and working standards using deionized water. Working standards of metal solutions were prepared in 50 mL volumetric flask by diluting with deionized water and the data are given in Table 2. Four points of calibration curve were establishing by running the prepared standard solutions in flame atomic absorption spectrometer. Figure 1 shows the linear correlation coefficient greater than 0.99 for all the analytes. Immediately after calibration, the sample solutions were aspired into the FAAS instrument and direct readings of the metal concentrations were recorded. Three replicate determinations were carried out on each sample. The analytical procedures were employed for the determination of elements in six blank samples. The operating conditions of FAAS for each analyte are given in Table 3.

Table 2. Concentration of standard solutions for FAAS instrument calibration and correlation coefficient of calibration curves.

Metal	Concentration of the standards in (ppm)	Correlation coefficient (R^2)
Cd	0.1, 0.2, 0.4, 0.8	0.99985
Cr	0.25, 0.5, 1, 2	0.99995
Cu	0.025, 0.05, 0.1, 0.2	0.99998
Fe	0.25, 0.5, 1, 2	0.99990

Pb	0.1, 0.2, 0.4, 0.8	0.99919
Zn	0.05, 0.1, 0.2, 0.4	0.99888
Na	0.125, 0.25, 0.5, 1	0.99988
K	0.5, 1, 2, 4	0.99988
Mg	0.5, 1, 2, 4	0.99973
Ca	0.5, 1, 2, 4	0.99986

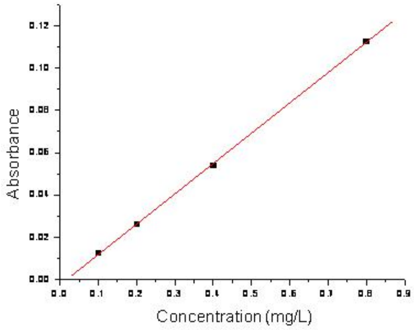

Figure 1a. Calibration graph of Cd

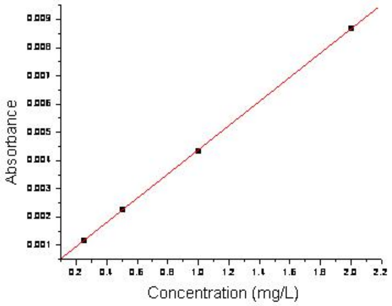

Figure 1b. Calibration graph of Cr

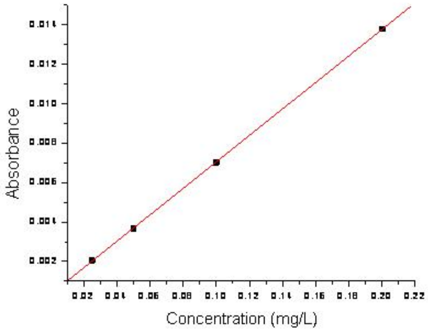

Figure 1c. Calibration graph of Cu

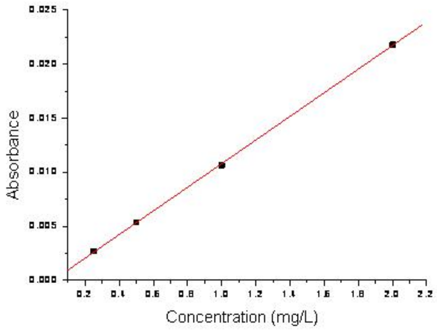

Figure 1d. Calibration graph of Fe

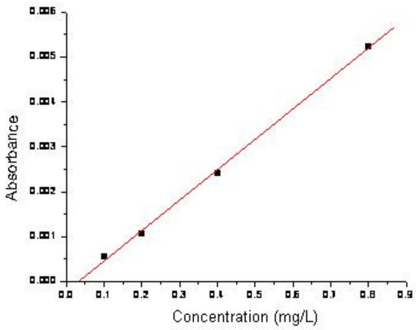

Figure 1e. Calibration graph of Pb

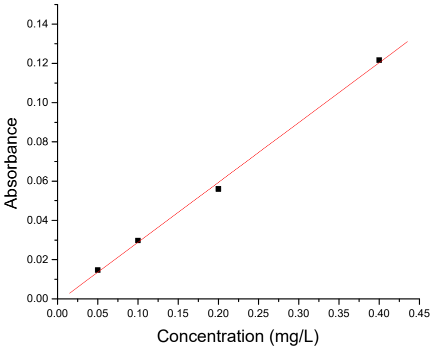

Figure 1f. Calibration graph of Zn

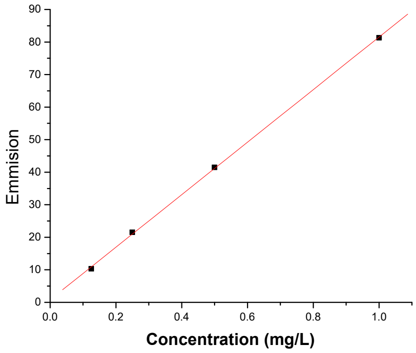

Figure 1g. Calibration graph of Na

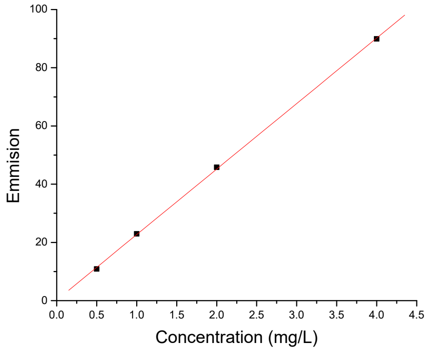

Figure 1h. Calibration graph of K

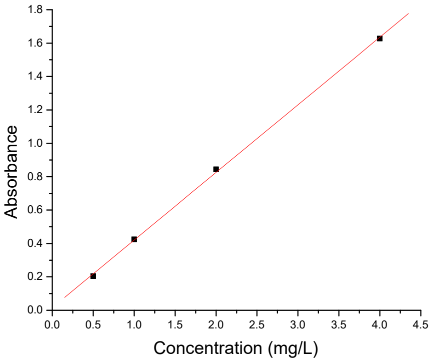

Figure 1i. Calibration graph of Mg

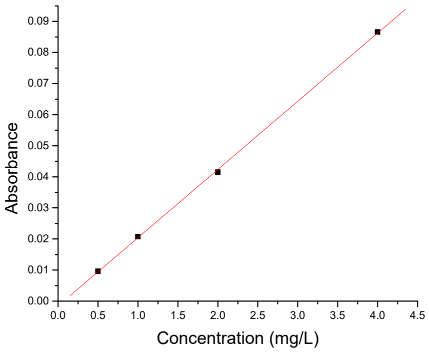

Figure 1j. Calibration graph of Ca

Figure 1. Calibration graphs of metals

Table 3. Instrument operating conditions for FAAS

Metal	Wavelength (nm)	Slit width (nm)	Current (mA)	Energy (eV)
Cd	228.9	0.7	2	3.359
Cr	357.9	0.7	2	3.697
Cu	324.7	0.7	1.5	3.316
Fe	248.3	0.2	7	3.609
Pb	283.2	0.7	2	3.532
Zn	213.9	0.7	2	3.126
Na	589.0	0.2	_	_
K	766.5	0.7	_	_
Mg	285.2	0.7	1	3.997
Ca	422.7	0.7	2	3.733

2.3.3 Analytical Procedures for Common Anions

The demand for the determination of ionic species in various water samples is growing rapidly along with increasing environmental problems, and it is clearly important to develop an appropriate analytical method for their determination. IC offers the most efficient method for determining ionic species in real natural waters [35, 36]. In the use of IC for analysis of common anions, optimization of operating conditions is very important and is given in Table 4 for anions. The column of the IC was washed by flushing deionized water for long time until the base line of the instrument obtained correctly up to zero background is obtained. The eluent of anions was degassed in the sonication bath and purged with argon gas for at least 10 min to remove dissolved gases. Composite standard solutions that were prepared from the primary standard solutions of anions were injected into the column the components were identified by comparison of retention time to the documented standards in the PeakNet6 software. After the instrument calibration was done with single point standard, the samples were added into vials and placed in the autosampler (Dionex AS50) that were ready for registration. The samples names and positions were registered manually on PeakNet6 software. All the programs were turned on and the samples were obeyed to run for in the determination of 10 min. As soon as the run was over, the chromatogram was displayed on PeakNet6 software and checked for each analyte whether the results were correctly obtained or not. The chromatogram of anion standards is shown in Figure 2. The peak area of the chromatogram was integrated and converted into concentration automatically by the instrument software and the results were recorded.

The pH of the samples was recorded on a pH meter (Jenway instruments, model 4330, Berkshire, UK) and the instrument was calibrated with pH 7.25 standard buffer solution. Electrical conductivity was measured with an EC model 214 conductivity meter (Hanna instrument, England) after standardizing with KCl and NaCl solutions.

Table 4. Instrument operating conditions and working standard solutions of anions for IC.

Injection volume (µL)	Concentration of anion (mg/L)	Peak name	Retention time (min)	Peak area (µS min)	Flow rate (mL/min)
25	2.0	F^-	1.75	0.010	1
25	10.0	Cl^-	2.01	0.040	1
25	10.0	NO_3^-	2.73	0.024	1

25	10.0	SO_4^{2-}	3.03	0.028	1
25	20.0	PO_4^{3-}	4.59	0.022	1

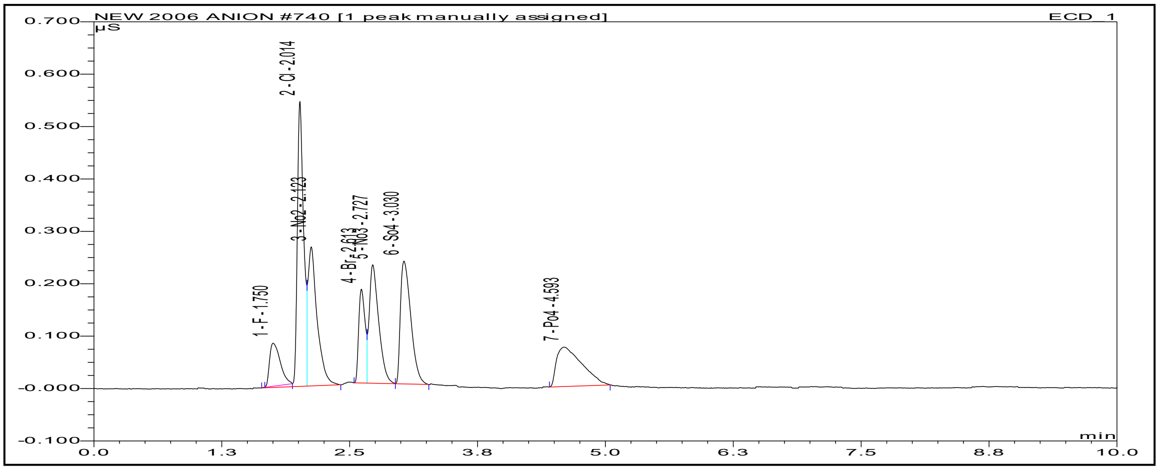

Figure 2. Chromatogram of anions standard solution

2.4 Determination of Limits of Detection

Limit of detection is defined as the minimum concentration of analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than Zero [37]. The general accepted definition of limit of detection is the concentration that gives a signal three times the standard deviation of the blank or background signal [38]. In this study limit of detection for the analysis of metals using FAAS in water samples were determined by using reagent blank, i.e. 1 mL of 69-72% HNO_3, which was used for acidifying the sample solutions, was added to 50 mL of deionized water that was used for washing apparatus and for the dilution of standard solutions. Then the method detection limit of each element was determined as three times the standard deviation of the blank solution ($3\sigma_{\text{Blank}}$, n = 6). The values were below the detection limit of the instrument; hence the instrument detection limit was taken for the determination of each metal except zinc (Table 5).

Sample preparation was not required for the analysis of common anions by IC. The water sample was directly taken from the bottles, injected to the column and analyzed. Thus the instrument detection limit (IDL) which is expressed as the smallest integrated area of the standard (0.001 μS/min) was used for the determination of anions.

Table 5. Instrument detection limits and limit of detection for the analysis of water samples by FAAS.

	Detection Limits	
Element	**IDL (mg/L)**	**LOD (mg/L)**
Cd	0.005	0.005
Cr	0.050	0.050
Cu	0.020	0.020
Fe	0.030	0.030
Pb	0.100	0.100
Zn	0.005	0.006
Na	0.002	0.002
K	0.010	0.010
Mg	0.001	0.001
Ca	0.010	0.010

3. RESULTS AND DISCUSSION

3.1 Accuracy and Precision of Results

The requirements of the analysis determine the best method. In choosing a method, consideration is given to accuracy and precision [40]. The analyst is thus concerned with the question of precision (repeatability of results) that is the agreement between the set of results. It can be determined by standard deviation, variance, relative standard deviation and range of series of measurements. In this study the precision of the results were evaluated by the pooled standard deviation and relative standard deviation of the results of triplicate samples with triplicate measurements of each sample ($n = 9$) were used for the analysis of metals in bottled water samples and standard deviation and relative standard deviation of the results of triplicate measurements ($n = 3$) were used for the analysis of common inorganic anions and two physical parameters. It can be observed from Table 6, Table 7 and Table 8 that the relative standard deviation values (% RSD) are less than 10% for all the mean concentrations.

3.2 Determination of Metals and Physical Parameters

The samples were analyzed for Cd, Cr, Cu, Fe, Pb, Na, K, Mg and Ca using flame atomic absorption spectrometer. The results are presented as the average of the determination of triplicate recording of the three sample solutions for each water samples. The results of metal concentration and two physical parameters are given in Table 6 and Table 7. During the analysis of seven drinking water samples, all the samples showed over range signal for sodium, Aqua Safe and Real Springs for potassium and Abyssinia, Aqua Safe, Kool and Real Springs for calcium. Therefore the above mentioned samples were diluted by appropriate factors. For the analysis of Na, the dilution factors of samples were 1:10 (Oasis, Real Springs and Tap water), 1:25 (Abyssinia, Aqua Safe and Kool) and 1:50 (Crystal); for potassium, 1:2 (Real Springs) and 1:5 (Aqua Safe) and for calcium 1:2 (Abyssinia, Kool and Real Springs) and 1:5 (Aqua Safe). After determination was over the results were calculated by multiplying by the dilution factors. No additional dilution of samples was performed for magnesium and all the trace heavy metals.

Table 6. The average concentration of trace metals in bottled and tap water samples

Sample	Concentration (mean ± SD) of metal (mg/L)					
	Cd	Pb	Cr	Cu	Fe	Zn
Abyssinia	< 0.005	< 0.1	< 0.05	< 0.02	0.055 ± 0.001	0.124 ± 0.002
% RSD	_	_	_	_	1.8	1.7
Aqua Safe	< 0.005	< 0.1	< 0.05	< 0.02	0.051 ± 0.003	0.088 ± 0.002
% RSD	_	_	_	_	5.1	2.3
Crystal	< 0.005	< 0.1	< 0.05	< 0.02	0.071 ± 0.002	0.293 ± 0.004
% RSD	_	_	_	_	2.9	1.5
Kool	< 0.005	< 0.1	< 0.05	< 0.02	0.049 ± 0.002	0.163 ± 0.006
% RSD	_	_	_	_	3.1	3.4
Oasis	< 0.005	< 0.1	< 0.05	< 0.02	0.035 ± 0.003	0.137 ± 0.006
% RSD	_	_	_	_	7.9	4.5
Real Springs	< 0.005	< 0.1	< 0.05	< 0.02	0.038 ± 0.003	0.096 ± 0.009
% RSD	_	_	_	_	8.1	9.3
Tap water	< 0.005	< 0.1	< 0.05	< 0.02	0.086 ± 0.006	0.334 ± 0.014
% RSD	_	_	_	_	7.1	4.0

Table 7. The average concentration of metals in (mg/L) and physical parameters in bottled and tap water sample

Sample	Concentration/values in the samples (mean ± SD)					
	Na	K	Mg	Ca	pH	EC (µS/cm)
Abyssinia	18.31 ± 0.216	2.22 ± 0.064	2.47 ± 0.139	6.80 ± 0.216	7.96 ± 0.057	229.7 ± 1.53
% RSD	1.18	2.88	5.63	3.18	0.72	0.67
Aqua Safe	23.20 ± 0.387	4.40 ± 0.044	1.91 ± 0.020	11.59 ± 0.250	8.34 ± 0.040	261.7 ± 4.73
% RSD	1.67	1.00	1.05	2.16	0.48	1.81
Crystal	48.03 ± 0.449	1.29 ± 0.121	2.13 ± 0.091	1.63 ± 0.150	7.49 ± 0.006	579.3 ± 11.68
% RSD	0.93	9.38	4.27	9.20	0.08	2.02
Kool	20.32 ± 0.541	1.19 ± 0.037	2.84 ± 0.015	5.10 ± 0.025	7.35 ± 0.040	124.3 ± 3.21
% RSD	2.66	3.11	0.53	0.49	0.54	2.58
Oasis	9.63 ± 0.150	1.89 ± 0.060	3.42 ± 0.025	2.01 ± 0.044	7.53 ± 0.021	160.7 ± 1.15
% RSD	1.56	3.17	0.73	2.19	0.28	0.72
Real Springs	7.69 ± 0.207	6.05 ± 0.113	1.30 ± 0.009	5.67 ± 0.224	8.05 ± 0.042	187.7 ± 1.53
% RSD	2.69	1.87	0.69	3.95	0.52	0.82
Tap water	2.77 ± 0.063	1.25 ± 0.034	3.37 ± 0.034	3.70 ± 0.051	7.83 ± 0.017	119.7 ± 0.58
% RSD	2.27	2.72	1.01	1.38	0.22	0.48

3.2.1 Determination of Metals

The concentration of elements Cd, Cr, Cu and Pb were below the detection limit in all the samples. Comparison of the metal contents in the water sample with WHO limit showed the mean levels of all the metals were below the maximum permissible level of drinking water. Thus all the samples of drinking water are safe to drink. Comparison of the concentration of each metal among the water samples is shown in Figure 3. Iron and zinc concentration levels are higher in tap water than the bottled water samples.

Cadmium: Concentration of cadmium was below the detection limit in all the water samples. WHO has recommended 0.003 mg/L of cadmium as the safe limit.

Contamination of drinking water may occur as a result of the presence of cadmium as an impurity in the zinc of galvanized pipes or cadmium-containing solders in fittings, water heaters, water coolers and taps [41].

Chromium: Chromium concentration was found below the instrument detection limit in all the analyzed water samples. The WHO guideline for chromium is set at 0.05 mg/L. Its toxicity related to the reduction of chromate to Cr^{3+} and radicals produced by the reaction. Most surface waters contain between 1 and 10 µg/L of chromium. In general, the chromium content of surface waters reflects the extent of industrial activity [42, 43].

Copper: Copper concentration was found below the instrument detection limit in all the analyzed bottled water samples. A safe limit set by the WHO regulation is 1 mg/L. Copper concentrations in drinking water vary widely as a result of variations in water characteristics, such as pH, hardness and copper availability in the distribution system [44].

Iron: Iron concentrations in the drinking water samples were in range of 0.035-0.071 mg/L. Iron was found at higher concentrations in the tap water than in bottled waters. The lowest content of iron was observed in Oasis. In all samples, the level of iron was below the proposed WHO guideline value of 0.3 mg/L. Concentrations of iron in drinking water are normally less than 0.3 mg/L but may be higher in countries where various iron salts are used as coagulating agents in water-treatment plants and where cast iron, steel, and galvanized iron pipes are used for water distribution [45].

Lead: Lead was found below the detection limit in all the bottled and tap water samples. According to WHO, the concentration of lead in drinking water should not exceed 0.01 mg/L. A major source of environmental Pb, particularly in urban areas, is due to the combustion leaded petrol. Lead then enters the waterways from soil, thus affecting the levels of lead in natural waters [17]. Lead is present in tap water to some extent as a result of its dissolution from natural sources but primarily from household plumbing systems in which the pipe, solder, fittings, or service connections to homes contain lead [46].

Zinc: The concentration of zinc in all samples was detected and found to be the largest than all the six trace metal analysed with the concentration range 0.088-0.334 mg/L. The minimum level of zinc was obtained in Aqua Safe. Zinc was found at higher concentration in tap water than bottled waters. None of the analyzed samples exceeded the levels of zinc set by the WHO (5 mg/L). Drinking water usually makes a negligible contribution to zinc intake unless high concentrations of zinc occur as a result of corrosion of piping and fittings [47].

Sodium: A wide range of concentrations was obtained for sodium, from 2.77-48.08 mg/L. The highest value was recorded for the Crystal. Three brands, Aqua Safe, Kool and Abyssinia, contain significantly higher concentrations of sodium (18.31-23.02 mg/L). The smallest concentration (2.77 mg/L) was found in the tap water. All the samples analyzed contain much lower level of sodium than the maximum permissible limit of 200 mg/L suggested by WHO. The sodium ion is ubiquitous in water. Most water supplies contain less than 20 mg of sodium per liter, but in some countries levels can exceed 250 mg/L [48].

Potassium: Values of potassium in analyzed samples range from 1.19-6.05 mg/L. Bottled waters (except Kool) contain slightly higher levels of potassium than tap water. No health-based guideline values are proposed for potassium. But based on Lau and Luk studies mineral waters with potassium exceeding 12 mg/L is not suitable for regular drinking because it may cause kidney stress and possible kidney failure [49]. Municipally treated drinking water may contain small concentrations of potassium. The use of a water softeners using potassium chloride can significantly increase the levels of potassium in drinking water, even at water hardness levels considered to be acceptable [26].

Magnesium: Concentrations of magnesium display a small diversity among samples, ranging from 1.30-3.37 mg/L. The only bottled water containing higher concentration than tap water was Oasis. No health-based guideline values are proposed for magnesium.

Calcium: Calcium concentration in all samples was less than 10 mg/L, except for the Aqua Safe (11.59 mg/L) sample. The lowest value was observed in Crystal water containing 1.63 mg/L. No health-based guideline values are proposed for calcium.

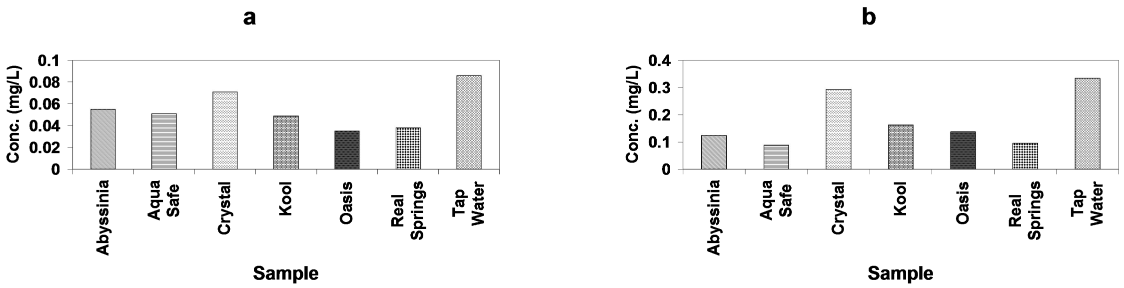

Figure 3a. Iron.

Figure 3b. Zinc

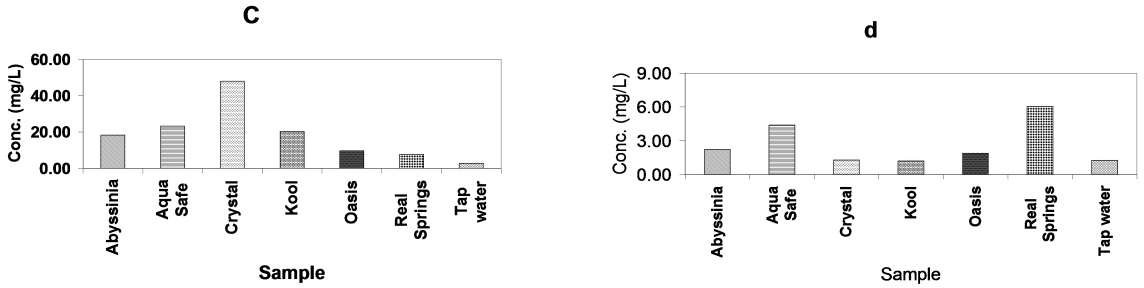

Figure 3c. Sodium

Figure 3d. Potassium

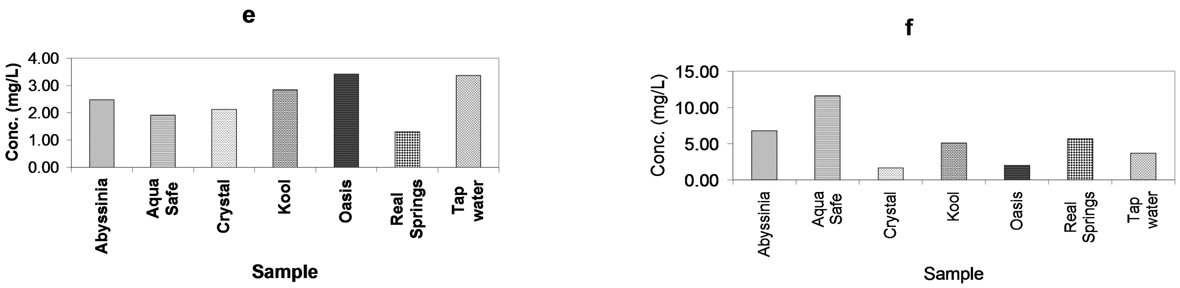

Figure 3e. Magnesium

Figure 3f. Calcium

Figure 3. Distribution of average concentration of metals in the bottled water samples

3.2.2 Determination Physical Parameters

The pH and the electrical conductivity (EC) are two important characteristic parameters for distinguishing differences among mineral waters. Comparison of the concentration of pH and EC among water samples is shown in Figure 4.

pH: The pH values were in the range of 7.35-8.34 (lowest in Kool, highest in Aqua Safe). No health-based guideline values are proposed for pH. According to ADWG and WHO, based on the need to reduce corrosion and encrustation in pipes and fittings, the pH of drinking water should be between 6.5 and 8.5 [9, 12]. Thus all the samples of drinking water were safe to drink.

Electrical Conductivity (EC): The ranges of electrical conductivity were 119.7-579.3 µS/cm. EC of crystal was much higher than other drinking water samples but the lowest EC value was obtained in tap water. The guide value is 2500 µS/cm [25].

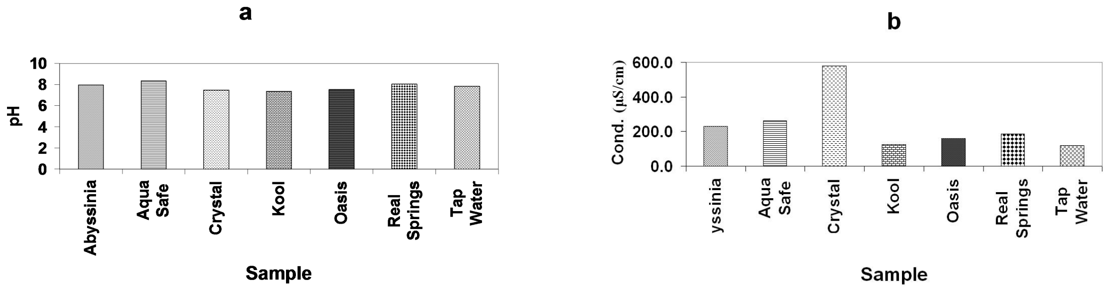

Figure 4a. pH

Figure 4b. Electrical conductivity

Figure 4. Distribution of average concentration of pH and electrical conductivity

3.3. Determination of Common Anions

In addition to being approved for a number of drinking water and wastewater analyses, IC is also widely used for analysis of natural water sample [50]. Determination of common anions was carried out by using DX-600 ion chromatography. It is capable of measuring a wide range of inorganic and organic ions, provided that there is an appropriate eluent and analytical column. Currently, common anions (F^-, Cl^-, NO_3^-, SO_4^{2-}

and PO_4^{3-}) using an Anion-Exchange CG17A column that is connected to guard columns was determined. For proper averaging of the chromatographic responses, injections for each sample were conducted in triplicate. The results were reported as the average of the triplicate results (n = 3) of each analyte in all samples. The results of these analyses are summarized in Table 8 and comparison of the concentration of each common anion among water samples is shown in Figure 4.

Table 8. The average concentration of common anions in (mg/L)

Sample	Concentration/values in the samples (mean ± SD)				
	F^-	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
Abyssinia	0.92 ± 0.036	8.31 ± 0.341	< 0.42	9.06 ± 0.230	< 0.91
% RSD	3.91	4.11	_	2.54	_
Aqua Safe	0.59 ± 0.025	12.38 ± 0.240	< 0.42	10.26 ± 0.169	< 0.91
% RSD	4.19	1.94	_	1.65	_
Crystal	< 0.20	6.15 ± 0.169	8.38 ± 0.266	< 0.36	< 0.91
% RSD	_	2.75	3.18	_	_
Kool	< 0.20	13.24 ± 0.218	2.80 ± 0.133	5.29 ± 0.184	< 0.91
% RSD	_	1.65	4.75	3.47	_
Oasis	0.25 ± 0.012	4.84 ± 0.079	6.02 ± 0.188	1.62 ± 0.071	< 0.91
% RSD	4.89	1.64	3.12	4.39	_
Real Springs	0.80 ± 0.034	10.79 ± 0.133	0.72 ± 0.034	0.99 ± 0.048	< 0.91
% RSD	4.25	1.23	4.79	4.83	_
Tap water	< 0.20	5.70 ± 0.197	1.67 ± 0.045	2.10 ± 0.083	< 0.91
% RSD	_	3.46	2.69	3.96	_

Fluoride: Average fluoride levels were found to be in the range of < 0.20-0.92 mg/L. Fluoride contents in three out of the seven water samples were below the detection limit. Abyssinia, Real Springs, Aqua Safe and Oasis were four brands that contained fluoride in the levels of 0.92, 0.80, 0.59 and 0.25 mg/L, respectively. The concentrations for all the samples were below the permitted levels of WHO (1.5 mg/L). In areas with relatively high fluoride concentrations in groundwater, drinking water becomes increasingly important as a source of fluoride [51].

Chloride: The highest chloride level was found in Aqua Safe as 12.38 mg/L and the lowest in Oasis as 4.84 mg/L. None of the drinking water samples analyzed for chloride exceeded the limit permitted by WHO (250 mg/L). Chloride in water may be considerably increased by treatment processes in which chlorine or chloride is used. If a daily water consumption of 2 L and an average chloride level in drinking water of 10 mg/L are assumed, the average daily intake of chloride from drinking water would be approximately 20 mg per person, but a figure of approximately 100 mg/day has also been suggested [52].

Nitrate: Nitrate in the investigated water samples was found in the range of < 0.42-8.38 mg/L. The highest value was obtained for Crystal whereas it was below the detection limit in Abyssinia and Aqua Safe. In all the samples, nitrate was found below the proposed WHO safe drinking water standards of 50 mg/L. The nitrate concentration in surface water is normally low (0–18 mg/L) but can reach high levels as a result of agricultural runoff, refuse dump runoff, or contamination with human or animal wastes. The concentration often fluctuates with the season and may increase when the river is fed by nitrate-rich aquifers [53].

Sulfate: Sulfate concentration in the drinking water samples were in range of < 0.36-10.26 mg/L. Generally higher values were observed in bottled waters than in tap water (except Real Springs and crystal). Sulfate was below the detection limit in Crystal. All the analysed samples contain very low levels of sulfate than the maximum permissible limit of 250 mg/L of WHO. The average daily intake of sulfate from drinking water, air and food is approximately 500 mg, food being the major source. However, in areas with drinking water supplies containing high levels of sulfate, drinking water may constitute the principal source of intake [54].

Phosphate: The levels of phosphate concentrations in all the investigated drinking water samples were below the detection limit. No health-based guideline values are proposed for the phosphate.

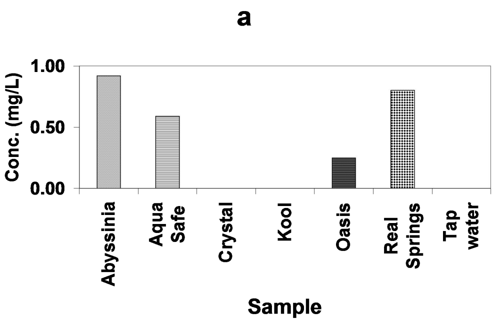

Figure 6a. Fluoride

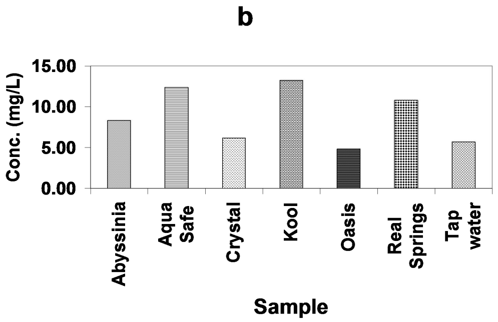

Figure 6b. Chloride

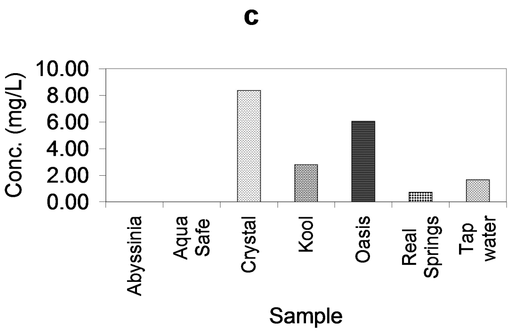

Figure 6c. Nitrate

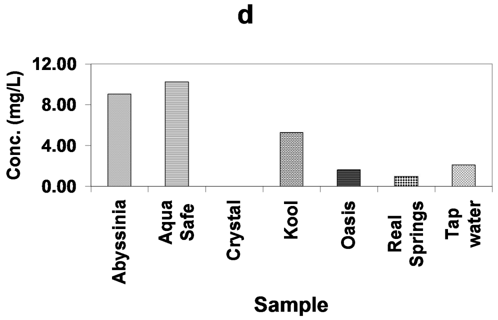

Figure 6d. Sulfate

Figure 5. Distribution of average concentration of common anions

3.4 Comparison of the results of present study with the labeled values

The results of present study were compared with that of labeled value using t-test and the results are given in Table 9. The t-test is a statistical tool used most frequently to express weather there is any significant difference between the true mean and the measured mean values of a given analytical data [55]. If the calculated t-value is greater than the critical t-value at some confidence level for a given degree of freedom, there is a significance difference between the true mean and measured mean. But if it is below the critical t-value, there is no significant difference between the mean values. In this study, Na, K, Mg, Ca and pH are labeled in the five brands (label of Crystal did not provide chemical analysis data). For that matter these listed species are compared by using t-test at 95% confidence level and 2-degree of freedom. The critical t-value for 95% confidence level and 2-degree of freedom is 4.30; the calculated value is compared with this critical t-value. Therefore there is a significant difference between the labeled values and the results obtained in these values.

Table 9. Comparison of analytes on the labels with present study in mg/L

Sample		Parameter				
		Na^+	K^+	Mg^{2+}	Ca^{2+}	pH
Abyssinia	Labeled value	34.1	5.4	3.4	12.0	7.4
	Present result	18.3 ± 0.2	2.22 ± 0.06	2.47 ± 0.14	6.80 ± 0.22	7.96 ± 0.06
	t-value	126.62	86.06	11.59	41.70	17.0
Aqua Safe	Labeled value	28.5	5	2.6	31.1	7.5
	Present result	23.2 ± 0.4	4.40 ± 0.04	1.91 ± 0.02	11.59 ± 0.25	8.34 ± 0.04
	t-value	23.72	23.62	114.32	135.17	36.4
Kool	Labeled value	35.0	3.5	2.8	10.9	7.25
	Present result	20.3 ± 0.5	1.19 ± 0.04	2.84 ± 0.02	5.10 ± 0.03	7.35 ± 0.04
	t-value	47.00	114.32	4.62	401.84	4.30
Oasis	Labeled value	15	3.1	5.1	4	6.72
	Present result	9.63 ± 0.15	1.89 ± 0.06	3.42 ± 0.03	2.04 ± 0.04	7.53 ± 0.02
	t-value	62.01	34.93	116.39	78.34	66.8
Real Springs	Labeled value	10.20	5.28	4	15.5	7.11
	Present result	7.69 ± 0.21	6.05 ± 0.11	1.30 ± 0.01	5.67 ± 0.22	8.05 ± 0.04
	t-value	21.00	11.80	519.62	76.01	38.8

3.5 Comparisons of Means in Composition of Bottled Water Samples of Present Study

The analysis of variance (ANOVA) test allows the judgment regarding the existence of significance difference in the precision between two sets of data [40]. ANOVA is an extremely powerfully statistical technique which can be used to separate and estimate the different causes of variation. In this study SPSS 13.0 for windows software was used to calculate the ANOVA for testing the significant differences in the composition of bottled waters. According to SPSS, to know the significant difference between the means of the determinations p-value will be considered. If the p-value obtained by calculation is less than 0.05, there is a significant difference between the means of the determination and if p-value is greater or equal to 0.05, there is no significant difference between means. Therefore in the comparison of the composition of mineral water samples, there were significant differences observed between the means of the determination for all the analytes except Fe concentration in Aqua Safe and Kool, Zn in Aqua Safe and Real Springs, K in Crystal and Kool, Ca in Crystal and Oasis, pH values in Abyssinia and Real Springs and Crystal and Oasis.

3.6 Comparison of Results of Present Study with Results from Other Countries

There are some reports from different countries on the analysis of mineral waters for the content of inorganic ions and physical parameters. It is important to compare the results obtained from the analysis of bottled waters in Ethiopia with that of worldwide countries to know the difference in the composition, suitability for drinking and their deviation from international guidelines that outlined for drinking water. The results of present study have been compared with the composition of mineral waters from twenty countries [49]. The comparison of current study was done by these reported results as a range of all the brands for each ion as given in Table 10. In this study six brands were analysed for common ions and trace heavy metals. With the exception of outlined results the composition of bottled water samples from different countries show more or less similar compositions.

Table 10. Comparison of the results obtained by present study with results from other countries in mg/L of analytes [49]

Country	Analyte							
	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
Ethiopia*	2.77-48.08	1.19-4.40	1.30-3.42	1.51-11.59	< 0.2-0.92	4.84-12.38	< 0.42-8.38	< 0.92-9.06
Egypt	4.49-169	0.11-18.5	1.54-23.3	1.39-44.8	0.12-0.48	11.1-221.1	0.1-18.7	10.4-68.12
Australia	2.4-34.5	0.7-20.0	5.7-38.6	0.5-4.6	0.10-0.22	5.9-47.4	0.6-24.8	0.7-6.8
Belgium	7.2-7.9	1.2-1.3	1.2	6.0	0.03-0.19	5.7-11.4	0.2-1.3	4.0-4.7
Canada	0.0-1.5	0.2-6.0	0.0-0.7	3.0-7.9	0.2-0.36	0.0	0.2-1.0	1.7-6.7
China	8.1-31.4	0.4-24.1	1.0-12.5	0.7-171.4	0.07-0.79	0.0-67.0	0.9-35.9	0.5-177.0
France	7.5-49.0	5.0-58.9	2.2-21.0	6.5-468.6	0.0-0.49	4.3-125.3	0.0-18.3	7.2-**1039.0**
Germany	**227.0****	170.5	50.5	113.0	0.0	45.8	1.1	47.0
Hong Kong	0.0-44.0	0.0-6.4	0.2-47.5	2.4-22.0	0.0-0.44	7.9-80.9	0.0-4.2	0.0-98.7
Iceland	14.7	1.1	0.0	4.7	0.04	15.9	0.7	2.6
Indonesia	9.1-40.0	4.3-70.7	2.8-10.3	2.8-21.4	0.0-0.31	0.0-26.4	0.7-38.1	1.3-27.2
Italy	3.3-30.9	0.5-26.5	0.8-48.0	6.3-40.0	0.0-1.2	0.0-19.4	5.1-9.1	4.8-41.5
Japan	7.9-8.4	0.9-2.8	0.4-2.1	0.4-2.1	0.0-0.02	3.0-7.8	0.5-1.5	0.4-2.3
Malaysia	5.8-30.8	0.0-3.4	4.0-5.8	4.9-18.3	0.05-**2.62**	2.9-22.9	0.0-13.5	0.9-3.2
Portugal	7.6-11.8	1.5-13.6	3.0-4.3	0.0-22.1	0.0-0.05	8.6-15.8	1.3-1.9	0.7-1.3
Scotland	8.1-58.0	13.3-17.9	2.9-3.1	47.7-110.0	0.05-0.1	8.6-138.6	1.1-4.8	0.8-8.0
Sweden	**225.0**	0.6	1.9	5.5	**2.4**	26.5	0.7	9.3
Thailand	68.0-69.2	0.2-14.9	15.1-25.0	31.6-38.0	0.03-1.81	30.7-133.2	0.2-0.4	1.7-33.9
Turkey	0.4	4.6	0.1	31.0	0.0	0.0	1.7	3.8
UK	10.3-30.0	1.4-26.0	0.8-5.0	54.6-140.0	0.0-0.1	15.1-33.5	0.3-15.0	3.6-70.0
USA	0.0-11.1	0.2-3.7	3.8-4.3	9.1-79.7	0.0-0.25	7.2-214.1	0.4-0.6	6.0-106.1

* Present work

** Value exceeding limit of standard

3.7 Comparison of Results of the Present Study with Some National and International Guidelines

WHO member states use the guidelines to develop their own standards but WHO encourages them to selective and to incorporate only relevant guidelines into standards. It also encourages member states to make adjustments to take into account local circumstances both in terms of drinking water intake, which varies in different parts of the world, and exposure to a contaminant from other sources than drinking water, particularly food [20]. WHO Guidelines are intended to apply to any drinking water but indicated, the Guidelines are not mandatory. In the European Union (EU) the directive on the quality of water intended for human consumption applies to “all water either in its original state or after treatment, intended for drinking, cooking, food preparation or other domestic purposes, regardless of its origin and whether it is supplied from distribution network, from a tanker, or in bottles or containers”. Guidelines and standards have the following functions: to protect public health and to ensure that drinking water is acceptable to consumers in terms of taste, smell, colour and clarity [10, 11].

In this study seven national and international guidelines in which the nations have developed their own standards depending upon the guidance of WHO guideline were considered for comparing the results obtained in this study to check weather the results are within the limits of guidelines of drinking water or not (for knowing the suitability of these water sample for drinking). The results are summarized in Table 11 (heavy metals) and Table 12 (common ions). These standard guidelines are WHO, Australia, Canada, USEPA, New Zealand, Pakistan and Codex. Based on these standard guidelines, the concentrations of investigated analytes in the drinking water samples are less than the permissible limits. Therefore all the water samples are safe for drinking.

Table 11. Comparison of results of present study (heavy metals) with some national and international guidelines

Guidelines	Analyte in mg/L					
	Cd	Pb	Cr	Cu	Fe	Zn
WHO [9]	0.003	0.01	0.05	2	0.2	5
Australia [12]	0.002	0.01	0.05	2	0.3	3
Canada [56]	0.005	0.01	0.05	≤ 1	≤ 0.3	≤ 5
USEPA [57]	0.005	0.005	0.05	1	_	5
New Zealand [17]	0.004	0.01	0.05	2	_	_
Pakistan [19]	0.003-0.01	_*	0.05-0.1	1-2	_	_
Codex [58]	0.003	0.01	0.05	1	_	_
Abyssinia	< 0.005	< 0.1	< 0.05	< 0.02	0.055	0.124
Aqua Safe	< 0.005	< 0.1	< 0.05	< 0.02	0.051	0.088
Crystal	< 0.005	< 0.1	< 0.05	< 0.02	0.071	0.293
Kool	< 0.005	< 0.1	< 0.05	< 0.02	0.049	0.163
Oasis	< 0.005	< 0.1	< 0.05	< 0.02	0.035	0.137
Real Springs	< 0.005	< 0.1	< 0.05	< 0.02	0.038	0.096
Tap Water	< 0.005	< 0.1	< 0.05	< 0.02	0.086	0.334

* The limit is not given

Table 12. Comparison of results of the present study (common ions) with some national and international guidelines

Guidelines	Analyte in mg/L								
	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
WHO [9]	200	_*	_	_	1.5	250	50	250	_
Australia [12]	180	_	_	_	1.5	250	50	500	_
Canada [56]	≤ 200	_	_	_	1.5	≤ 250	45	≤ 500	_
USEPA [57]	_	_	_	_	2.0	_	10	250	_
New Zealand [17]	_	_	_	_	1.5	_	_	_	_
Pakistan [19]	_	_	_	_	1.5-4.0	250-400	_	_	_
Codex [58]	_	_	_	_	2	_	50	_	_
Abyssinia	18.31	2.22	2.47	6.80	0.92	8.31	< 0.42	9.06	< 0.91
Aqua Safe	23.0	4.40	1.19	11.59	0.59	12.38	< 0.42	10.26	< 0.91
Crystal	48.03	1.29	2.13	1.63	< 0.20	6.15	8.38	< 0.36	< 0.91
Kool	20.32	1.19	2.84	5.10	< 0.20	16.24	2.80	< 0.36	< 0.91
Oasis	9.63	1.89	3.42	2.01	0.25	4.84	6.02	1.62	< 0.91
Real Springs	7.69	6.05	1.30	5.67	0.80	10.79	0.72	0.99	< 0.91
Tap Water	2.77	1.25	3.37	3.70	< 0.20	5.7	1.67	2.10	< 0.91

* The limit is not given

4. CONCLUSION AND RECOMMENDATION

The drinking water analysis for physical, chemical properties including trace elements are very important for public health studies. The determinations of metals and common anions were performed using FAAS and IC, respectively. The mean values were calculated with only values above detection limit. Concentrations of Cr, Cd, Cu, Pb and PO_4^{3-} were below the detection limit in all the samples.

Among six heavy metals, only Fe and Zn were detected and by comparing bottled and tap waters, higher values were obtained in tap water. The Na and K levels were significantly higher in bottled waters than tap water. A small range of concentration was obtained for Mg. The anion concentrations were varying among the samples, however, higher values were obtained for bottled waters than tap water.

This study has shown that the entire water samples meet the national and international limits for the trace metals and common ions. It means that the bottled waters are safe to drink. However, regular monitoring and periodically testing for chemical compositions should be ensured by the authorities concerned.

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