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DETERMINATION OF COMMON IONS AND HEAVY METALS IN BOTTLED MINERAL WATER CONSUMED IN ADDIS ABABA (ETHIOPIA)

By

Tolera Seda

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DEDICATED TO

MY WIFE SOLENI GUTEMA

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LISTS OF ACRONMS AND ABBREVIATIONS

FAAS	Atomic Absorption spectrometer
IC	Ion Chromatography
DBPs	Disinfectant By-Products
WHO	World Health Organization
USEPA	United State Environmental Protection Agency
EPA	Environmental Protection Agency
EC	European Commission
EEC	European Economic Community
ISO	International Organization for Standardization
MCL	Maximum Contaminant Level
TDS	Total Dissolved Solid
NTP	National Toxicology Program
IARC	International Agency for Research on Cancer
CAC	Codex Alimentarius Commission
%RSD	Percentage Relative Standard Deviation
SD	Standard deviation
ND	Not Detected
ANOVA	Analysis of Variance
DF	Degree of Freedom

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By: Tolera Seda

Advisors: Prof. B.S. Chandravanshi and Dr. Mesfin Redi

ABSTRACT

The inorganic compositions of three (Ambo, Aquaddis and Highland) brands of bottled mineral water and tap water samples from different sources that are consumed in Addis Ababa (Ethiopia) were analyzed using standard methods. FAAS was used for the determination of four heavy metals (Fe, Cr, Cd and Zn); Cd and Cr were not detected in all samples. Ion chromatography was used for the determination of common cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) and common anions (F^-, Cl^-, Br^-, NO_3^-, $SO_4^{2-}$and PO_4^{3-}) in the bottled mineral water and tap water samples. Common cations were found to be higher in Ambo mineral water than other two mineral water samples, some of the anions were not detected in some of the mineral water samples; phosphate was not detected at all. The composition of the mineral waters was also compared with that of the tap water. Fe and Zn were higher concentration in tap water as compared to mineral waters and the reverse was true in the case of common cations and anions. Some brands of bottled mineral water with respect to some of the analytes were found not to comply with international guidelines for drinking water and may not be suitable for babies and people suffering from heart or kidney diseases. Some physical parameters, pH and electric conductivity of each water sample were determined; pH in some samples found to be below the lower limit of WHO guideline.

Keywords: FAAS, IC, Bottled mineral water, Heavy metals, Common cations and anions, Physical parameters.

1. INTRODUCTION

Water is essential for life on earth. Because of its importance, the pattern of human settlement throughout history has often been determined by its availability [1]. Next to oxygen, water is the most important substance for human existence [2]. It is an essential nutrient, which also sustains agriculture, allows aquatic life, supports industry, produces hydroelectricity, permits aquatic transport, insures personal hygiene, maintains clean environment, and is used for sport as well as for recreation [3, 4]. Certainly, man gets the benefits listed above from the entire water resources of the world which is estimated to be 1.4 x 10^9 km^3 [5]. However for the most part human existence mainly depends on fresh water supply which is less than 1% of the water available on earth [6]. The fresh water of the world is obtained from the annual precipitation of about 10^5 km^3 [7] out of which Ethiopia's yearly share is estimated to be 110 km^3 [3]. However, 75% of this water vanishes through the borders toward neighboring countries leaving behind 27.5 km^3. On the other hand, since this water is not evenly distributed, arid and semiarid regions of the country are threatened by desertification [8]. In addition to the process of desertification, pollution is also reducing the volume of safe drinking water. For instance a report revealed that consumption of sea-food products had led to increased morbidity and mortality [9]. Likewise cancer mortality due to exposure of ground water to hazardous chemicals is increasing [10]. If heavy metals present in drinking water, they may lead to severe effects that include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system [11]. Toxic metals can be present in industrial, municipal, and urban runoff, which can be harmful to humans and aquatic life. Increased urbanization and industrialization are to blame for an increased level of trace metals, especially heavy metals, in our waterways. There are over 50 elements that can be classified as heavy metals, 17 of which are considered to be both very toxic and relatively accessible. Toxicity levels depend on the type of metal, it's biological role, and the type of organisms that are exposed to it. The heavy metals linked most often to human poisoning are lead, mercury, arsenic and cadmium. Other heavy metals, including copper, zinc, and chromium, are actually required by the body in small amounts, but can also be toxic in larger doses.

1. 1. Literature Review

The quest for high-quality water has been an objective of human society going back to prehistoric times. Early humans gathered in locations with readily accessible sources of water and if the water was believed to be of questionable quality, entire settlements would be abandoned. The first documented drinking water treatment can be found in Egyptian hieroglyphics, describing procedures to purify water. The basic principles were the same then as they are today; boiling, chemical treatment and filtration were recommended treatments. Although the importance of drinking water quality was known, the specific contaminants would not be identified for centuries to come.

The importance of clean water, clean air and safe working conditions spawned the public health era in the mid 1850s. From this concern grew the science of epidemiology, with the landmark investigation of a cholera outbreak by John Snow [12]. From that filtration treatment for improving drinking water quality paralleled studies establishing the link between disease and water quality. The introduction of chlorine as a chemical disinfectant was an alternative for those communities that could not afford the expense of elaborate filtration plants. The introduction of chlorination of drinking water was followed by a remarkable reduction in cholera, dysentery and typhoid worldwide. Today, water treatment and specifically chlorination and/or filtration of drinking water have been haled as the major public health achievement of the 20th century [13]. As the century progressed, the identification of water contaminants shifted from microbiological to chemical. As the public health infrastructure grew, outbreaks associated with chemical spills or leaks into potable water drew the attention of the scientific community. Concern with inorganic contaminants such as arsenic, lead, copper and sulfate began to be reported in the epidemiologic literature [14]. In the mid-1970s, two events occurred that spurred the health concern of chemicals in water. The first was a reporting of chloroform in finished water treated by chlorine especially along the Mississippi River in the United States [15]. The second was a series of mortality maps showing higher cancer mortality rates in those communities [15, 16]. In the following years, the number of chemical contaminants identified in drinking water has grown exponentially. However, for the hundreds of chemicals identified, very few have been studied or have documented proof of their health effects in humans via ingestion of contaminated water. Of the few for which a body of epidemiologic literature exists, the interpretation of the data is often confusing and controversial given the chemical of concern.

1.1.1 Sources of Contaminants in Drinking Water

There is no such thing as naturally pure water. In nature, all water contains some impurities. As water flows in streams, sits in lakes, and filters through layers of soil and rock in the ground, it dissolves or absorbs the substances that it touches. Some of these substances are harmless. In fact, some people prefer mineral water precisely because minerals give it an appealing taste. However, at certain levels of minerals, just like man-made chemicals, are considered contaminants that can make water unpleasant or even unsafe. A number of chemical contaminants have been identified in drinking water. The chemical contaminants for which epidemiologic studies have suggested a risk associated with their presence in potable water include: aluminum, arsenic, disinfection by-products (DBPs), fluoride, lead, nitrate, pesticides, cadmium, mercury and sulfate. The contaminants are of both inorganic and organic origin. The source of the contaminant can be from point and non-point sources of pollution, naturally occurring, come from the treatment process or through materials used in distribution systems [12]. Naturally occurring contaminants are generally the result of leaching from geologic formations and are found primarily in groundwater. Ranges of concentrations of these contaminants range from less than nanograms per litre (ng/L) to milligrams per litre (mg/L). Point sources of drinking water contaminants include direct dumping of chemicals from domestic and industrial sewage. Other sources of pollution include runoff from land application of chemicals or leaching from buried solid waste landfills. Finally, mining practices or smelter operations can increase the concentrations of metals in source waters through the atmospheric deposition or improper handling of mining tailings. The treatment process can be a significant source of chemical contaminants. Disinfectants themselves are not believed to be a significant health hazard at levels used to treat water for drinking. The disinfectants (primarily chlorine or chlorine based), because of their strong oxidizing properties, react with the other organic constituents in the water to form chlorinated or brominated compounds believed to be of major toxicological concern. Aluminum and fluoride are both added to the treatment process but are not believed to be of concern at the levels they are added to water for treatment. It is when they are present as the result of geological leaching that concern has been raised. Contaminants can occur because of the distribution system or materials that comprise the distribution system. As the result of corrosion or leaching of distribution materials, many of the materials can be found as chemical contaminants in potable water.

1.1.2 Health Effects of Contaminants in Drinking Water

Chemical contaminants occur in drinking water supplies throughout the United States, ranging from barely detectable amounts to levels that could possibly threaten human health. Determining the health effects of these contaminants is difficult, especially since researchers are still learning how chemicals react in the body to damage cells and cause illness [12].

As mentioned previously, concern with chemicals in drinking water started in outbreak situations where individuals became acutely ill. Chemical spills or leaks still occur causing acute like toxicity (primarily vomiting). As more chemicals could be found in potable water, studies began to appear in the literature linking health effects with occurrence of the contaminant of interest. Cancer has been one of the more popular endpoints to study in relationship to effects associated with exposure to specific chemicals in water. Recent years have seen an interest in reproductive and developmental effects. Studies of cancer and reproductive effects have been aided by the existence in many communities of databases of mortality or morbidity for these endpoints. The epidemiologic evidence in conjunction with toxicological data (human and animal) has been considered important in establishing causal relationships between the exposure and effects for arsenic, lead, nitrate, radon, etc. [17].

Toxic doses of chemicals cause either acute or chronic health effects. An acute effect usually follows a large dose of a chemical and occurs almost immediately. Examples of acute health effects are nausea, lung irritation, skin rash, vomiting, dizziness and even death. The levels of chemicals in drinking water, however, are seldom high enough to cause acute health effects. They are most likely to cause chronic health effects -effects that occur after long exposure to small amounts of a chemical. Examples of chronic health effects include cancer, birth defects, organ damage, disorders of the nervous system, and damage to the immune system. Evidence relating chronic health effects to specific drinking water contaminants is limited. In the absence of exact scientific information, scientists predict the likely adverse effects of chemicals in drinking water using laboratory animal studies and, when available, human data from clinical reports and epidemiological studies [18].

1.1.3 Potable Water

Good-quality drinking water may be consumed in any desired amount without adverse effect on health. Such water is called ‘potable’. It is free from harmful levels of impurities such as bacteria, viruses, minerals, and organic substances. It is also aesthetically acceptable and is free of unpleasant impurities, such as objectionable taste, color, turbidity, and odor. As fresh water supplies are further stretched to meet the demands of industry, agriculture and an ever-expanding population, the shortage of safe and accessible drinking water will become a major challenge in many parts of the world. In the wake of several major outbreaks involving food and water, there is a growing concern for the safety and quality of drinking water. While bottled water is widely available in both industrialized and developing countries, it may represent a significant cost to the consumer. Consumers may have various reasons for purchasing bottled drinking water, such as taste, convenience or fashion, but for many consumers, safety and potential health benefits are important considerations. The most common problems in household water supplies may be attributed to hardness, iron, sulfides, sodium chloride, acidity, and disease-producing pathogens, such as bacteria and viruses [1].

The purity of drinking water also depends on the sources and water type. The water used may be from any source, including spring water, well water purified water, municipal water, or even untreated or contaminated water [12]. Because of the large number of possible hazards in drinking water, the development of standards for drinking water requires significant resources and expertise, which many countries are unable to afford. Fortunately, guidance is available at the international level. The World Health Organization (WHO) publishes guidelines for drinking-water quality which many countries use as the basis to establish their own national standards. The guidelines represent a scientific assessment of the risks to health from biological and chemical constituents of drinking water and of the effectiveness of associated control measures. 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 [19]. Many countries regulate the quality of bottled water through government standards, typically used to ensure that water quality is safe and labels accurately reflect bottle contents [20]. In many developing countries, however, such standards rarely exist, or are inconsistently applied.

1.1.4 Bottled Mineral Water

Bottled water usually tastes better than what comes out of tap [21]. Public water systems generally are disinfected with chlorine. Bottled water is commonly disinfected by ozone treatment. Ozone is high-strength oxygen that quickly reverts to normal oxygen. It is a strong oxidant, like chlorine, but does not add taste like chlorine does. The length of time chlorine and ozone remain active in water depends on many factors, including temperature. Chlorine usually provides residual disinfection throughout the public-water distribution system. Ozone provides a residual disinfection for a limited time. However, bottled water may be in distribution for several weeks and storage conditions, especially temperature, may adversely affect quality. In terms of bacterial content, it is questionable as to whether bottled water is better than most municipal tap water. Bottled water often is purchased for its good taste. However, taste does not always indicate safeness. At the concentrations present in drinking water, most harmful substances (including some disease-causing microorganisms, nitrates, trace amounts of lead and mercury, and some pesticides and organic materials) have no taste. Differences in taste among bottled waters generally are due to differing amounts of carbon dioxide, calcium, iron compounds, sodium, and other minerals and mineral salts. Differences also may be due to the amount and type of processing.

In Canada consumable water is generally classified into three categories: drinking water i.e. tap water, bottled mineral (spring) water and other bottled water, i.e. distilled waters, flavored waters, reverse osmosis water. The last two classes (bottled mineral water and other bottled water) fall under the prepackaged designation in accordance with the Canadian food and drug regulation [22]. In Malaysia all bottled waters are classified as natural mineral water, spring water and bottled drinking water [23]. Natural mineral waters are officially recognized sources of underground water which have to be naturally free from pollution, harmful micro-organisms and be stable in mineral analysis and it must be bottled at source. The water may not be treated in any way intended to alter its natural microbiological or chemical composition. Spring waters are subjected to most of the same requirements as natural mineral waters except the recognition procedure. They must be from a single named underground source and be bottled at source. All other bottled drinking waters are usually referred to as 'Table Waters' and do not need to come from a single source or go through a source recognition procedure. They do however have to meet the same microbiological and chemical standards of bottled Spring Water [24].

Mineral water and spring water contain various mineral salts, especially the carbonates, chlorides, phosphates, silicates, sulfides, and sulfates of calcium, iron, lithium, magnesium, potassium, sodium, and other metals. Various gases may also be present, e.g., carbon dioxide, hydrogen sulfide, nitrogen, and inert gases. Ordinary well or spring water, in contrast, contains far fewer substances, mostly dissolved sulfates and carbonates, and calcium and other alkali and alkaline earth metals. Many mineral waters are now prepared synthetically, the various mineral ingredients being added to ordinary water in proportions determined by careful chemical analysis of the original ingredients.

In European and certain other countries, many consumers believe that natural mineral waters have medicinal properties or offer other health benefits [23]. Such waters are typically of high mineral content and, in some cases, significantly above the concentrations normally accepted in drinking water. Such waters have a long traditional use and are often accepted on the basis that they are considered foods rather than drinking water. Although certain mineral waters may be useful in providing essential micro-nutrients, such as calcium, however, WHO is unaware of any convincing evidence to support the beneficial effects of consuming such mineral waters. As a consequence, WHO Guidelines for Drinking water Quality do not make recommendations regarding minimum concentrations of essential compounds.

Reports from different countries have shown that the content of some of the bottled mineral water has been compared with that of the World Health Organization (WHO) guideline. For example, in Egypt five brands of bottled mineral water were analyzed and all water samples were within the acceptable levels of the World Health Organization (WHO) guidelines and were lower than maximum contaminant levels (MCL) established by the United States Environmental Protection Agency (USEPA) [1]. In the same way in Malaysia, fifteen locally available natural mineral waters including samples from French and Thailand origin (M14 and M15) respectively were analyzed for cations and anions [25]. On the whole, the amounts of anions found were of slightly lower concentration than the values claimed by the companies. In brand M10, they found that it contains19.2 mg/L of nitrate but the concentration of this anion was not stated on the bottle while, in brand M13, the magnesium content was found to be about five times the value stated on the bottle. Of the eight anions and cations determined in the report, only fluoride and nitrate are regulated by Malaysian Food Act 1983. In Britain, scientists at the University of Wales at Aberystwyth tested 81 bottled waters, selected at random, for their mineral content using a plasma mass spectrometer [26]. Many were found to have levels of potentially harmful minerals which were above the legal regulation levels for tap water. In some cases they were considerably higher. The legal limit for sodium in tap water is 150 mg/L. The amount of sodium in Vichy Saint-Yorre, for example, was seven times that limit. For anyone on a low-salt diet, this is much too high. In Hépas, calcium was nearly twice the limit and fluoride in Mattoni was more than twice the limit. In Canada, forty domestic and imported brands of bottled water were purchased in Manitoba and examined for total dissolved solids (TDS), chloride, sulfate, nitrate–nitrogen, cadmium, lead, copper, and radioactivity [27]. The samples showed great variation in quality, and some exceeded the Canadian Water Quality Guidelines for drinking water for TDS, chloride, and lead. Carbonation, ozonation, and type of packaging were not associated with differences in metal levels, although carbonated samples tended to show higher TDS values. A number of deficiencies were found with respect to product labeling

International standards for bottled drinking water: the intergovernmental body for the development of internationally recognized standards for food is the Codex Alimentarius Commission (CAC). WHO, is one of the co-sponsors of the CAC, has advocated the use of the guidelines for drinking-water quality as the basis for derivation of standards for all bottled waters. The CAC has developed a Codex Standard for natural mineral waters and an associated code of practice. The Codex Standard describes the product and its labeling, compositional and quality factors, including limits for certain chemicals, hygiene, packaging and labeling. The Codex Code of Practice for collecting, processing and marketing of natural mineral waters provides guidance to the industry on a range of good manufacturing practices matters. While CAC standards and recommendations are not strictly mandatory, Codex health and safety requirements are recognized by the World Trade Organization as representing the international agreement for consumer protection and any deviation from Codex recommendations may require a scientifically-based justification. This commission is currently developing a draft of a Codex Standard for Bottled/Packaged Waters to cover drinking-water other than natural mineral waters.

According to CODEX standard [28], natural mineral water used as a food is defined as water clearly distinguishable 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 other constituents. It is obtained directly from natural or drilled sources from underground water bearing strata for which all possible precautions should be taken within the protected perimeters to avoid any pollution or external influence. It is collected under conditions which guarantee the original microbiological purity and chemical composition of essential components, it is packaged close to the point of emergence of the source with particular hygienic precautions and it is not subjected to any treatment other than those permitted by this standard.

A naturally carbonated natural mineral water: is a natural mineral water which, after possible treatment by decantation or filtration, and after packaging has the same content of carbon dioxide spontaneously and visibly given off under normal conditions of temperature and pressure.

A non-carbonated natural mineral water: is a natural mineral water which, by nature and after possible treatment, does not contain free carbon dioxide in excess of the amount necessary to keep the hydrogen carbonate salts present in the water dissolved.

A decarbonated natural mineral water: is a natural mineral water which, after possible treatment by decantation and/or filtration and after packaging, has less carbon dioxide content than that at emergence and does not visibly and spontaneously give off carbon dioxide under normal conditions of temperature and pressure.

A natural mineral water fortified with carbon dioxide from the source: is a natural mineral water which, after possible treatment by decantation and/or filtration, and after packaging, has more carbon dioxide content than that at emergence.

A carbonated natural mineral water: is a natural mineral water which, after possible treatment and after packaging, has been made effervescent by the addition of carbon dioxide from another origin.

According to CODEX standard, [29] the maximum contaminant levels of some common contaminants in bottled drinking water are given in Table 1.

Table 1. CODEX standard of maximum contaminant levels in drinking water

Substances	Maximum concentration level (mg/L)	Substances	Maximum concentration level (mg/L)
Antimony	0.005	Fluoride	1.5
Arsenic	0.01	Lead	0.01
Barium	0.7	Manganese	0.15
Borate	5	Mercury	0.001
Cadmium	0.003	Nickel	0.02
Chromium	0.05	Nitrate	50
Copper	1	Nitrite	0.02
Cyanide	0.07	Selenium	0.01

1.1.5. Metals in the Diet

Varieties of metals are found in a range of foods in the diet, and in this context, are termed minerals, along with some non-metals, such as iodine and fluorine. These minerals can be macro minerals those that are needed by the body in relatively large amounts, e.g. sodium, potassium, chlorine, calcium, phosphorus and magnesium. It presents in virtually all cells of the body, maintaining general homeostasis and required for normal functioning [30, 31]. Acute imbalances of these minerals can be potentially fatal, although nutrition is rarely the cause of these cases. Diet can affect levels of macronutrients in the body, but effects are generally chronic, e.g. a high intake of sodium can lead to hypertension [32]. And micro/trace minerals are those needed in small amounts, e.g. selenium, iron, zinc, copper, manganese, molybdenum, chromium, arsenic, germanium, lithium, rubidium and tin. Many of these minerals have been classed as essential elements; necessary for utilization by the body to ensure good health, but the function of these minerals and their benefits to the body is still uncertain and has been widely speculated. It contributes to good health if they originate from an organic source because they have essentially been processed. Plants take up minerals from the ground, digest them, making them ionic so that when consumed by humans, assimilation into the body occurs much more easily, and toxicity by accumulation does not occur. However, micro minerals from inorganic sources, such as heavy metals, can not be used by the body as they tend to build up in the tissues [33].

Much research has been carried out; concerning the role of minerals in the body, but in many cases, difficulties in investigating their individual effects has been expressed because intake is often in combination with other vitamins and minerals [34], e.g. fruit and vegetables contain several minerals. There is, however, strong evidence that supplementation of certain minerals would benefit those suffering from deficiency disorders. It is also important to note though that intake of minerals does not necessarily correlate with absorption and a balance must be obtained.

1.1.6. Mineral Salts and Oligoelements in Water

The water formula is H_2O, two atoms of hydrogen and one atom of oxygen but only distilled water has this structure. Rain water, snow and ice are quite similar to distilled water. Water presents in nature contains, even if in traces, minerals very important for our health: salt and oligoelements dissolved during its way through the soil or it's flowing in rocky streams [35].

Calcium: Calcium is one of the most common elements on the earth [36]. It is essential in our body for teeth and bones formation, blood coagulation, right functioning of our nervous system. Calcium ions are contained in almost all spring drinking water. Health effects caused by hard water, very rich in calcium and magnesium, are unknown [37]. An excess in calcium can alter the water taste or cause scaling problems in pipes and household appliances. In the reduction of the content of calcium and magnesium ions dissolved in water it is recommended that the calcium content never goes under 60 mg/L. The World Health Organization has recommended a minimum calcium daily intake of about 700 mg. Drinking calcium poor water is considered dangerous for the risk of coronary diseases.

Magnesium: Magnesium is, with sodium and calcium, among the cations most commonly found in drinking water. In humans magnesium is important for many metabolic functions and for muscular and nervous activity [36]. The daily recommended intake is 150-500 mg.

Sodium: Sodium is an element very diffused on earth and in the biosphere, even if in nature it is almost never in its pure form, but mainly in form of salt (NaCl). Our body contains an average of 100 g of sodium which is an important metabolic regulator for nervous and muscular stimulations. The daily sodium chloride intake is 200 mg. Due to our diet very rich in salt it is recommended to drink water with sodium content lower than 20 mg/L, particularly for hypertension people and children. The salt consumption in industrialized countries is considered much higher than the recommended levels (about 3.9 g/day on average) [38]. Drinking 2 liters of water containing 20 mg/L of sodium you reach 40 mg that is about the 5% of the total intake. To reduce the daily sodium intake it would be more logical to change your nutrition, i.e. to eat only integral sea salt, more equilibrate and rich in mineral salts at home, and to avoid precooked food, always rich in refined salt.

Chromium: Chromium is an important oligoelement for our organ, on condition that certain concentration is not exceeded and the element is not found in toxic or carcinogenic combinations (always due to industrial pollution). Chromium speciation in environmental samples is of interest, because its toxicity to aquatic and terrestrial organism depends on the oxidation number of chromium. Chromium is an industrially important metal, which has the potential to contaminate drinking water sources. Chromium (VI) is more water soluble, more easily enters living cells, and is much more toxic than chromium (III). Chromium (VI) is a human carcinogen, as determined by the National Toxicology Program (NTP), the International Agency for Research on Cancer (IARC), the U.S. Environmental Protection Agency (USEPA). Chromium enters environmental waters from anthropogenic sources such as electroplating factories, leather tanneries and textile manufacturing facilities. Chromium also enters groundwater by leaching from soil [39].

Iron: Food rich in iron is very important, particularly for children and women in fertile age. The recommended daily intake is 10 mg. Iron is usually contained in low amount in drinking water. The WHO has recommend a maximum of 2mg/L the EEC of 0.2 mg/L. Possible increasing (lower than 200 mg/L) are not to be considered harmful, even if they make the water not nice to drink and give an unpleasant reddish colour.

Chlorine: At present chlorination is the most used treatment to remove water bacteria which could cause health problems. The Italian law allows 30 mg/L of chlorine, while the guidelines of the European Directive indicate 1 mg/L and specify that the concentration should be as low as possible. According to international research the consumption of water containing compounds formed after the reaction between chlorine and micro organisms (trihalometanes) can contribute to the increasing of hurogenital tumours. When the tap is opened the smell of chlorine odour typical of swimming pools is recognized, it is recommended to pour the water in a large tank and to leave it open or semi-open for about half an hour. Chlorine is in fact very volatile and tends to still on the water surface. To accelerate chlorine dispersion one can pour the water from a tank to another repetitively or mix very quickly [40].

Fluorine: In someone opinion fluorine is useful for the good health of bones and teeth, sometimes it is even essential, in others opinion it is unnecessary when you are adult, above all if it is added. Fluorine is an halogen and it is the most electronegative of all the elements, so it reacts easily with most of the elements. In 1945 the addition of fluorine in drinking water began to be experimented in New York State, followed by Australia and some areas in UK, with the declared purpose of preventing dental caries in population [40]. Water fluorination is prohibited in Belgium, Denmark, the Netherlands and France; in Spain and Germany local authorities handle every decision and in Italy there is no specific law on this matter. Fluorine values useful for our body are very close to toxic values, so a dispense not aimed and personalized can cause high risk of overdosing and chronicle poisoning, with consequent skeleton deformation, spots on tooth enamel, neurological disorders, damages on the thyroids and even tumours. Fluorine has negative effects on the central nervous system, determining behaviour alterations, cognitive deficit, influencing on the foetus development even in concentration not harmful for the mother.

Zinc: Zinc is one of the most common elements in the earth's crust. It is also an essential element for all living things [41]. Pure zinc is a bluish-white, shiny metal. Zinc has many commercial and industrial uses. A large proportion of all zinc, perhaps more than a third, is used to galvanize metals such as iron so as to prevent corrosion. Zinc metal is used for dry batteries, roof cladding, and to protect iron structures from corrosion by attaching zinc as sacrificial anodes [42]. Zinc is mixed with other metals to form alloys such as brass and bronze, and pennies are made from a copper-zinc alloy. The oxide (ZnO) is also combined with other elements such as chlorine, oxygen, and sulfur to form zinc compounds used to make white paints, ceramics, rubber, wood preservatives, dyes, and fertilizers. Zinc compounds are also used in the drug industry as ingredients in common products like sun blocks, diaper rash ointments, deodorants, athlete's foot preparations, and anti-dandruff shampoos. The sulfide (ZnS) is used in making luminous dials, X-ray and TV screens, paints and fluorescent lights. According to EPA, in natural surface waters, the concentration of zinc is usually below 10 μg/L, and in ground waters, 10–40 μg/L. In tap water, the zinc concentration can be much higher as a result of the leaching of zinc from piping and fittings. The most corrosive waters are those of low pH, high carbon dioxide content, and low mineral salts content. Zinc is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes.

The diet is normally the principal source of 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. The 1958 WHO international standards for drinking water suggested that concentrations of zinc greater than 15 mg/L would markedly impair the potability of the water. The 1963 and 1971 international standards retained this value as a maximum allowable or permissible concentration. In the first edition of the guidelines for drinking water quality, published in 1984, a guideline value of 5.0 mg/L was established for zinc, based on taste considerations. The 1993 guidelines concluded that, taking into account recent studies on humans, the derivation of a guideline value was not required at this time. However, drinking-water containing zinc at levels above 3 mg/L may not be acceptable to consumers [43].

1.1.7 Other Inorganic Toxic Substances

Many toxic minerals are contained in water supplies, usually at high levels. Treatment and potabilisation plants work very well reducing these minerals to safe levels. Minerals can enter surface or ground water through natural sources, industrial sewage, and leakage from urban or agricultural areas, water pipes walls or even from domestic sources

Aluminium: Aluminium is very abundant on the earth, but is not important for human nutrition. Aluminium can have toxic effects even in small quantities [44]. These effects occur in nervous system, but health effects originating from aluminium intake through water are still on debate. Aluminium concentration is usually lower than 200 mg/L in drinking water. If you drink 1.5 litre of water per day, your daily intake from water is lower than 300 mg/day, a negligible amount if compared with the amount taken by nutrition (10-20 mg/day). There is no evidence that the aluminium consumed through water is more soluble and then more easily digestible, than the aluminium contained in food. Due to all these uncertainties at present there are no rules about its concentration allowed in drinking water. The WHO recommends a concentration lower than 20 mg/L.

Arsenic: Arsenic can be toxic even in low amounts. Nevertheless the arsenic contained in food (amounts ranging from 0.01 to 1.5 mg/kg of dry weight) has a different influence: it carries out some positive metabolic function for our body. Its toxicity is strongly linked on the concentration [44].

Cadmium: Cadmium is a highly toxic heavy metal, considered carcinogen. Its harmful action is similar to the effect of lead and it can be released in drinking water by zinc and iron pipes. Zinc always contains a small amount of cadmium [45].

Lead: Lead is poisoning even in small amounts for microorganisms, interfering with haemoglobin formation and with the functionality of central nervous system. Lead is particularly harmful for children, who can suffer long term neurological and behavioural disorders. Major lead sources are paint, vehicle emissions, food and water. The WHO guideline about drinking water for human consumption states that the maximum allowed lead concentration in drinking water should not exceed 0.015mg/L and some precautions can be taken to lower lead content in drinking water [46].

Phosphate: In the body, phosphorus is combined with oxygen to form a variety of phosphates (PO_4^{3-}). Phosphates are vital for energy production, muscle and nerve function, and bone growth. They also play an important role as a buffer, helping to maintain the body's acid – base balance. About 70% to 80% of the phosphates are combined with calcium to help form bones and teeth, about 10% are found in muscle, and about 1% is in nerve tissue. The rest is found within cells throughout the body, where it is mainly used to store energy; about 1% of total body phosphate is found within plasma. Most phosphate in the body comes from dietary sources. A variety of foods, such as beans, peas and nuts, cereals, dairy products, eggs, beef, chicken, and fish contain significant amounts of phosphate. The body maintains phosphate levels in the blood by regulating how much it absorbs from the intestines and how much it excretes or conserves in the kidneys. Phosphate in water originates from detergents and fertilizers and a level higher than 0.1 mg/L indicates pollution [EPA 1998].

Sulphates: Sulphates are sulphuric acid salts combined with metallic ions. Water can naturally contains small quantities of sulfates, but they are mostly transferred in water bodies from the atmosphere and in the atmosphere from road traffic, industries and energetic production. Sulphur oxidised in the air can come back on the soil as acid rain causing serious environmental problems. Sulfate is a substance that is occurs naturally in drinking water. Health concerns regarding sulfate in drinking water have been raised because of reports of diarrhea associated with the ingestion of water containing high levels of sulfate. Of particular concern are groups within the general population that may be at greater risk from the laxative effects of sulfate when they experience an abrupt change from drinking water with low sulfate concentrations to drinking water with high sulfate concentrations [47].

Nitrates and Nitrites: Nitrates are the main source of nitrogen for plants and an essential constituent for nucleic acids and amino acids. A nitrate water content of about 10 mg/L is considered normal and natural. Different concentration is due to human operations (mauring, air pollution due to transport). The problems resulting from excessive nitrate presence are due to the toxicity of nitrate for human body: nitrates are transformed in nitrites or in carcinogenic nitrosamines.

1.2 Bottled Mineral Water Consumed in Addis Ababa

Addis Ababa is the capital city of Ethiopia. The populations of the city are over 3.5 million and live in 10 sub-cities and 204 districts divided for administrative purposes. It is situated at 9 ^{o}N and 38 ^{o}E and lies between 2200 and 2500 meters above sea levels on a well-watered plateau surrounded by hills and mountains [48]. It is an administrative and communications center of the country and also the main trade center for coffee, chat, grains, and hides which are the agricultural and industrial products that used for country's chief export. Addis Ababa has a large tourist industry. The African Union and the UN Economic Commission of Africa are headquartered in the city which also hosts numerous international conferences. It is the center of a highway network and a terminus of a railroad that runs to Djibouti, making Addis Ababa an important distribution center. The well known international airport of the country is situated in Addis Ababa. There is also large number of hotels, restaurants, recreational place for wedding ceremonies and for other purposes.

In this capital city of Ethiopia different brands of indigenously produced bottled mineral waters are available in local markets and restaurants. These bottled mineral waters are used by many Ethiopians and tourists visiting Ethiopia for satisfying their water requirement and enjoyment purposes. Most of these known mineral water are Ambo natural mineral water, Highland spring water, Aquaddis spring water, Abyssinia spring water, Aqua Safe natural mineral water, Kool natural mineral water, etc. Out of the above bottled mineral waters, the first three are the most commonly consumed bottled mineral water by many people in Addis Ababa. Ambo mineral water is the oldest and the known mineral water, which is distributed throughout the country by 500 mL sized glass bottles. The location of source for this mineral water is the underground mineral water of Ambo that bottled at source. The type of analysis for this mineral water is determination of the chemical composition of the water in mg/L. Highland is another mineral water consumed in Addis Ababa which is recently developed industrial product, but has high demand for drinking and entertainment by tourists and local people and it is distributed by plastic bottles of different size (with 500 mL and 1 L). The sources of the water are deep protected aquifer from highland of Ethiopia. Water analysis is given as chemical composition in mg/L. It is bottled at source by Apex Bottling Company. The third important bottled mineral water consumed in Addis Ababa is Aquaddis natural spring water which is newly developed industrial product which also has high demand for drinking. The location of source of this mineral water is from natural source of Burayu highland. It is bottled at source by Burayu Spring water PLC.

Advertisement for bottled mineral water in Addis Ababa shows mineral water is better than tap water for drinking. However, the regulations on 'Spring Waters' may seem relaxed. Hence 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. And it is likely to be contaminated. Therefore it is important to determine and compare the content of mineral waters consumed in Addis Ababa with that of worldwide standards in general and the ions listed on labels of bottled mineral water in particular. In this particular research the concentration of selected pollutants in three brands of the most common commercial bottled drinking water (Ambo, Highland, and Aquaddis) are presented. For comparison purpose samples of tap water was collected from three pipe location in Arat Kilo Campus of Addis Ababa University. This research is carried out to clarify some of the concerns about the quality and safety of bottled drinking water which practically costs much higher than public drinking water.

1.3 Objective of the Research

1.3.1 General Objective

The main objective of this research project is to determine common ions and heavy metals in bottled mineral water consumed in Addis Ababa.

1.3.2 Specific Objectives

1. To determine cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Cr^{3+}, Cd^{2+}, Zn^{2+}) and anions (Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, PO_4^{3-}, F^-, Br^-) in the mineral water samples (Ambo mineral water, Highland spring water, Aquaddis mineral water).

2. To determine cations and anions in the Addis Ababa municipal tap water.
3. To compare the levels of cations and anions in the municipal tap water and the mineral waters.
4. To compare the levels of cations and anions in the mineral waters consumed in Addis Ababa (Ethiopia) with that in the other countries in the world.
5. To compare the levels of cations and anions in the municipal tap water and the mineral waters consumed in Addis Ababa with the World Health Organization and other world water bodies guidelines for drinking waters.

2. EXPERIMNENTAL

2.1 Instrumentation and Apparatus

For the analysis of bottled mineral water and tap water samples that are consumed in Addis Ababa, two methods were selected. For the determination of heavy metals (iron, chromium, cadmium and zinc); flam atomic absorption spectroscopy (FAAS) was selected following the recommendation of the U.S. Environmental Protection Agency. And for the analysis of major cations (sodium, calcium, magnesium, potassium) and common anions (sulfate, phosphate, nitrite, fluoride, chloride and bromide); 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

For the analysis of heavy metals (Fe, Cr, Cd, and Zn) by FAAS, BUCK SCIENTIFIC MODEL 210VGP (East Norwalk, USA) Atomic Absorption Spectroscopy equipped with deuterium ark background correctors, cathode lamps for each respective element, and air-acetylene flame were used.

IC Apparatus

For the analysis of common cations (Na^+, Mg^{2+}, K^+, Ca^{2+}) and common anions (SO_4^{2-}, PO_4^{3-}, NO_2^-, F^-, Cl^-, Br^-); 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 ºC Built-in electrochemical cell. And Autosampler (Dionex AS50) was used for sample preparation and temperature control. Isocratic separation of both cations and anions were performed on IonpacCS12A cation exchange column-Atlas suppressor, IonpacCS12A analytical column (4 x 250 mm)-046073, and IonpacAS17 anion exchange column-Atlas electrolytic suppressor, IonpacAS17 analytical column (4 x 250 mm)-

055682, respectively. Dedicated IonpacCG12A guard column (4 x 50 mm)-046074 for cationic and IonpacAG17 guard column (4 x 50 mm)-055684 for anions were also used in connection with the analytical columns. Dionex GS50 Gradient pump and EG40 eluent generator containing cartridge-058900 for generating eluent to the separator system were used for the analysis of both anions and cations. 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 heavy metal elements (iron, chromium, cadmium, zinc) HNO_3 (69-72%) was used for acidifying the sample solutions, deionized water was used for washing apparatus and for dilutions of standard solutions. Stock solutions of the metals (Fe, Cr, Cd, Zn) 1000 mg/L (calibration standard Buck Scientific, USA, prepared as nitrates for each element in 2% HNO_3) were used for the preparation of calibration curves for the determination of metals in the mineral water samples.

In the analysis of common ions (calcium, magnesium, sodium, potassium, sulfate, phosphate, nitrate, fluoride, chloride, and bromide) by ion chromatography, H_2SO_4 (20 mM) DBH limited pool, England was used as mobile phase for eluting cations while KOH (20 mM) DBH limited pool, England was used as mobile phase for eluting the anions. Composite primary standard solutions of cations that contains (200 mg/L sodium, 500 mg/L potassium, 250 mg/L magnesium and 500 mg/L calcium) was used for the analysis of cations which was prepared from chloride salts of the cations by using ultra pure deionized water (99.78% water) and similarly composite standard solution of anions that contains (20 mg/L fluoride, 100 mg/L chloride, 100 mg/L nitrate, 100 mg/L Bromide, 100 mg/L sulfate and 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. The working standard solution of anions then contains 2 mg/L fluoride, 10 mg/L chloride, 10 mg/L sulfate, 10 mg/L nitrate, 20 mg/L phosphate and similarly that of cations contains 50 mg/L calcium, 25 mg/L magnesium, 50 mg/L potassium and 20 mg/L sodium 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

Three brands of the most popular bottled mineral water samples: Ambo, Highland and Aquaddis mineral water that are consumed in Addis Ababa (Ethiopia) were purchased from local supper markets around Arat Kilo. Three bottles of 500 mL size were purchased for each brand in the determination of heavy metals (Fe, Cr, Cd, and Zn). Two brands (Highland and Aquaddis) mineral waters are sold in sealed plastic bottles and one brand (Ambo) mineral water is sold in sealed glass bottle. All bottles were kept sealed and refrigerated at 4 ^{o}C until the time of analysis. Tap water samples were randomly collected from three different pipe locations in Arat Kilo (Addis Ababa University, Science Faculty Campus) by 1 L volumetric flask for the comparison purpose. Each water sample was collected from tap water used for drinking in the campus that was left running for more than 5 min before collecting the sample. The collected tap water samples were kept in the sealed flasks and refrigerated with that of bottled mineral waters at the same temperature until the time of analysis. All the samples were analyzed for heavy metals (Fe, Cr, Cd, Zn) by FAAS within 12 days from the time of sample collection. All samples were filtered using Whatman filter paper to remove the bubble from the samples 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 refrigerator for analysis.

For the determination of common cations and anions using ion chromatography three bottles for each brands were purchased from the same supermarkets. Tap water was also collected from three different pipe location and the samples were refrigerated until complete analysis of all samples were done. The sealed bottles were newly opened and directly analyzed without any pre-treatment of the sample.

2.3.2 Analytical Procedures for Heavy Metal Analysis

In this study, the concentrations of a number of heavy metals (iron, chromium, cadmium, and zinc in most popular commercially available bottled mineral water available in Addis Ababa (Ambo, Aquaddis, and Highland mineral waters) and tap water samples were quantitatively determined using FAAS as mentioned in section 2.3.1. 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 established by running the prepared standard solutions in flame atomic absorption spectrometer. Figure 1 shows the linear correlation coefficient greater than 0.999 for all the analytes. Immediately after calibration, the sample solutions were aspirated into the FAAS instrument and direct readings of the metal concentrations were recorded. Three replicate determinations were carried out on each sample. The same analytical procedures were employed for the determination of elements in eight blank samples. The operating conditions of FAAS are given in Table 3.

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

M	Concentration of the standards in (mg/L)	Correlation coefficient
Fe	0.2, 0.4, 0.8, 1.6	0.9993
Cr	0.1, 0.2, 0.4, 0.8	0.9990
Cd	0.1, 0.2, 0.4, 0.8	0.9999
Zn	0.1, 0.2, 0.4, 0.8	0.9998

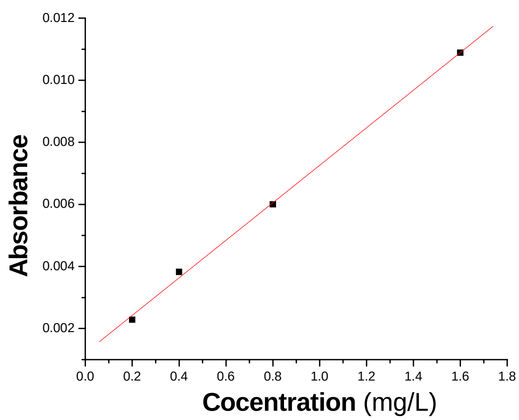


Fig. 1a. Calibration curve of Fe.

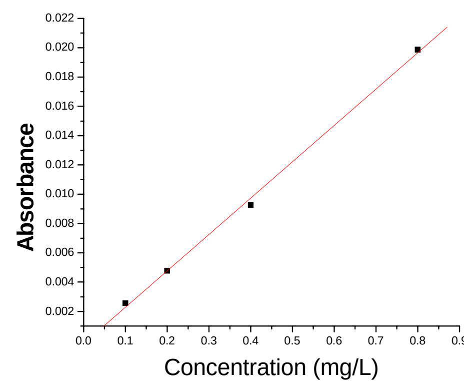


Fig. 1b. Calibration curve of Cr.

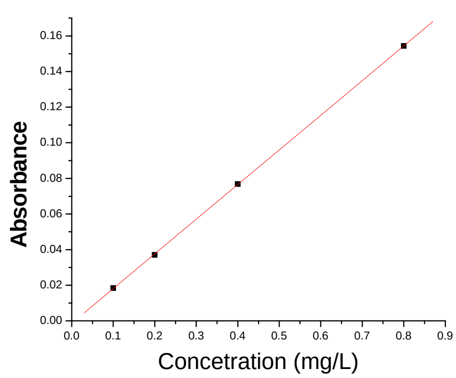


Fig. 1c. Calibration curve of Cd.

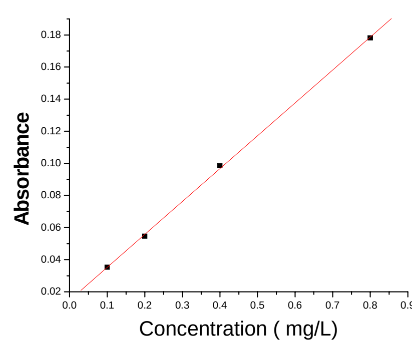


Fig. 1d. Calibration curve of Zn.

Table 3. Instrument operating conditions for FAAS.

Element	Wavelength (nm)	Detection limit (mg/L)	Slit width (nm)	Current (mA)	Energy (EV)
Fe	248.3	0.03	0.2	7	3.735
Cr	357.9	0.05	0.7	2	3.759
Cd	228.9	0.005	0.7	2	3.338
Zn	213.9	0.005	0.7	2	3.312

2.3.3 Analytical Procedures for Determination of Common Cations and Anions

Bottled mineral water and tap water samples were analyzed for common ions using ion chromatography. In ion chromatography, retention is based on the attraction between solute ions and charged sites bounded to the stationary phase (ion exchange resins) frequently made by copolymerization of styrene and divinyl benzene. The benzene rings in divinyl benzene can be modified to produce either cation exchange resin (containing negatively charged groups) or anion exchange resin (containing positively charged groups) [49]. In the use of IC for analysis of major cations and anions, optimization of operating conditions is very important and is given in Table 4 and Table 5 for cations and anions, respectively. The column of the IC was washed by flushing deionized water for long time until the base line of the instrument obtained correctly or up to zero background is obtained. The eluent of both cations and anions were degassed in 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 cations and anions were injected into the column. The components were identified by comparison of retention times to documented standards in the PeakNet6 software. After the instrument calibration was done with single point calibration standard, the samples were added into vials and placed in the autosampler (Dionex AS50) that were ready for registration. The sample names and positions were registered manually on PeakNet6 software. All the programs were turned on and the samples were obeyed to run for 10 min in the determination of anions and 15 min for that of cations. As soon as the run was over, the chromatogram was displayed on PeakNet6 software and checked for each analyte weather the results were correctly obtained or not. The chromatograms of standard are shown in Figure 2 and 3 for cations and anions, respectively. 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 measured using Denver Instrument model 250, pH-ISE conductivity meter that was calibrated with pH 10.01 standard buffer solutions. The conductance of each sample solution was also measured using ion conductivity electrode with standard buffer solutions and the results are presented in Table 8.

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

Injection volume (µL)	Amount (mg/L)	Peak name	Ret. Time (min)	Peak Area (µS*min)	Flow Rate
25	20.0	Na	4.48	0.085	1 mL/Min
25	50.0	K	6.30	0.132	1 mL/Min
25	25.0	Mg	9.87	0.141	1 mL/Min
25	50.0	Ca	11.75	0.216	1 mL/Min

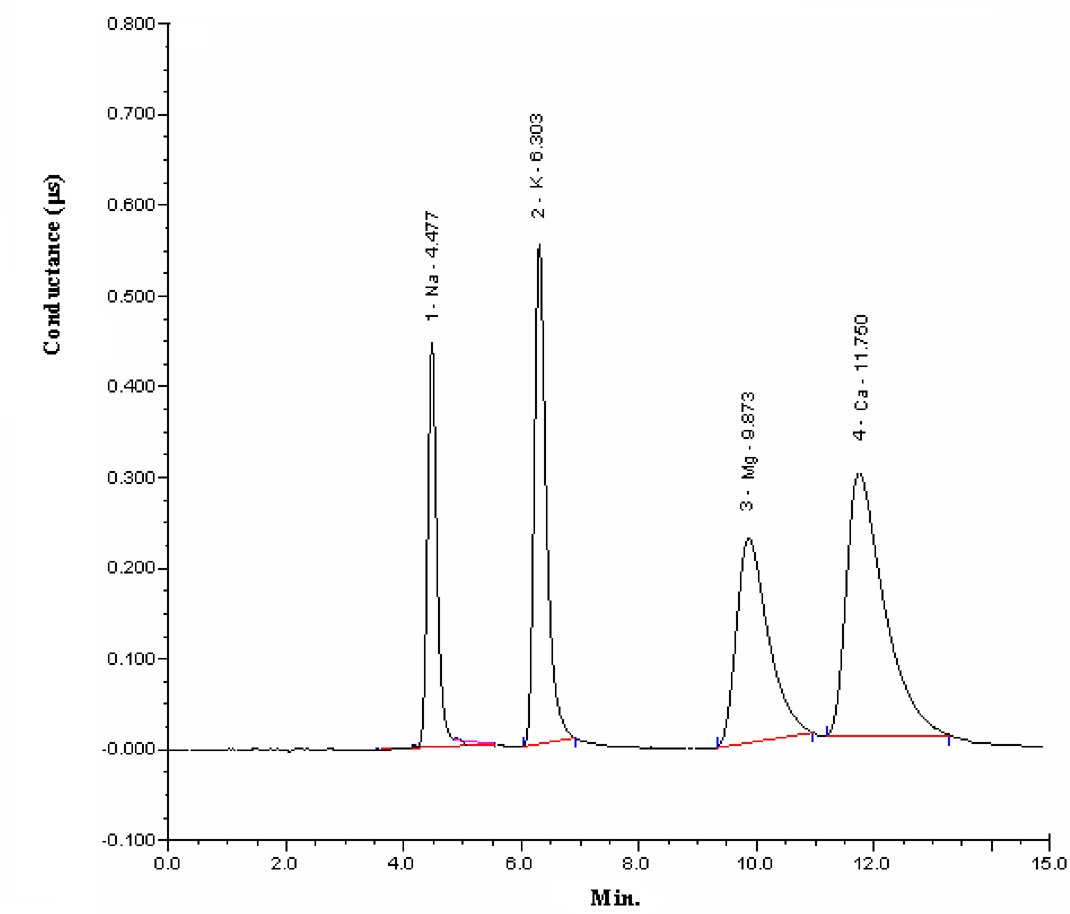


Fig. 2. Chromatogram of standard solution of cations.

Table 5. Instrument operating conditions and working standard solutions of anions for IC.

Injection volume (µL)	Amount (mg/L)	Peak name	Ret. time (min)	Peak Area (µS*min)	Flow Rate
25	2.0	F^{-}	1.77	0.006	1 mL/Min
25	10.0	Cl^{-}	2.09	0.028	1 mL/Min
25	10.0	Br^{-}	2.82	0.005	1 mL/Min
25	10.0	NO_3^{-}	2.95	0.029	1 mL/Min
25	10.0	SO_4^{2-}	3.49	0.017	1 mL/Min
25	20.0	PO_4^{3-}	5.56	0.012	1 mL/Min

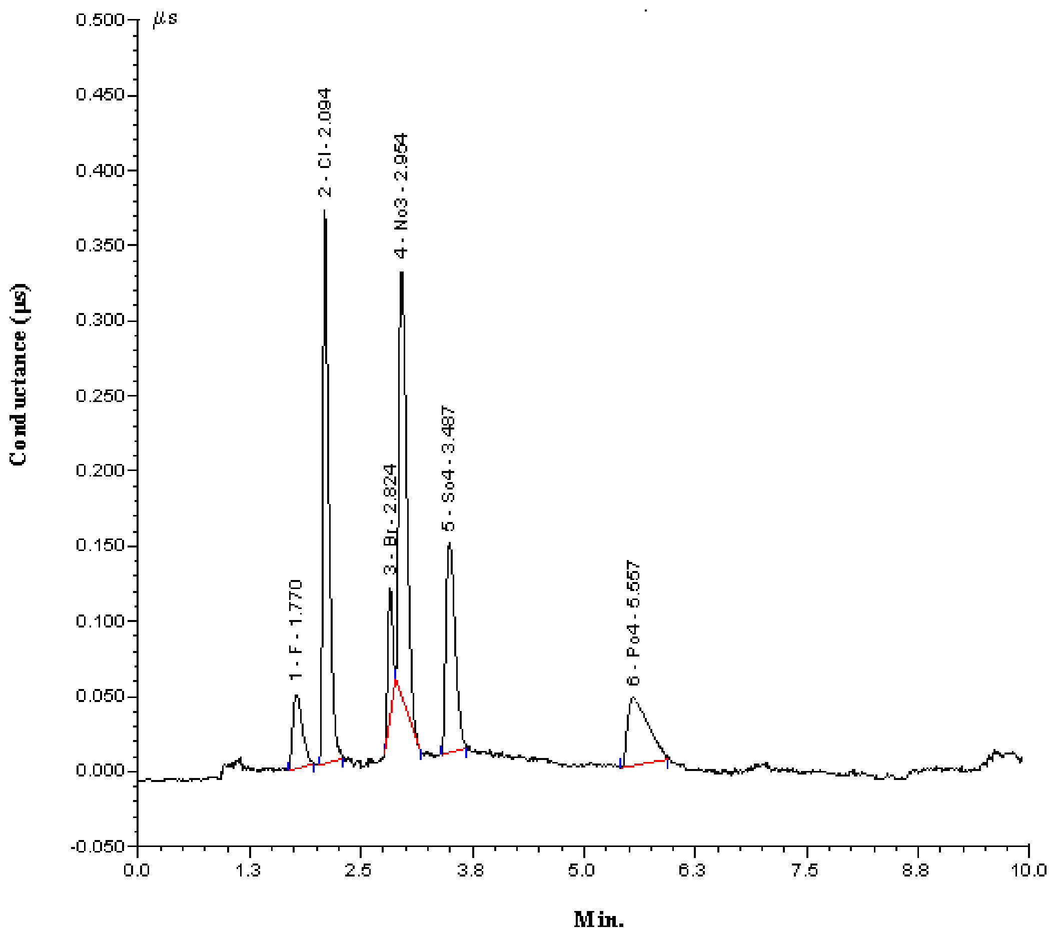


Fig. 3. Chromatogram of the standard solutions of anions.

2.4 Determination of Method Detection Limits

Method detection limit 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. The general accepted definition of method detection limit is the concentration that gives a signal three times the standard deviation of the blank or background signal [52].

In this study method detection limit for the analysis of heavy metals using FAAS in water samples were determined 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 ($3\sigma_{Blank,}$ n = 24). The value was below the detection limit of the instrument; hence the instrument detection limit was taken for the determination of each metal (Table 6).

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

Table 6. Instrument method detection limits for the analysis of water samples by FAAS.

Detection limits		
Element	**IDL (mg/L)**	**MDL (mg/L)**
Fe	0.03	0.03
Cr	0.05	0.05
Cd	0.005	0.005
Zn	0.005	0.005

3. RESULTS AND DISCUSSION

3.1 Accuracy and Precision of Results

Accuracy and precision are probably the most often quoted terms to express the extent of errors in a given analytical results. Analytical results must be evaluated to decide on the best values to report and attempt to establish the probable limits of errors of the values [50]. The analyst 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, coefficient of 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 heavy metal cations in mineral 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 ions and some physical parameters. It can be seen in Table 7 and 8 that the values of relative standard deviations (% RSD) are less than 10% for all the mean concentration except for the concentration of Zn^{2+}, and Mg^{2+}, in Ambo (13.5, and 11.8, respectively), Cl^{-}, Br^{-} and SO_4^{2-} in Highland (12.9, 13.8 and 12.5, respectively), Cl^{-} in Aquaddis (12.9) and Br^{-}, $NO_3^{-}$and SO_4^{2-} in tap water (10.9, 11.3 and 12.1, respectively) all of these values are below 15 %. This shows that the precision of the results obtained in both methods (FAAS and IC) are good.

3.2 Determination of Heavy Metals

Analysis of water samples was carried out using two methods as mentioned in the experimental part of this study. Four heavy metals (Fe, Cr, Cd and Zn) were determined using flame atomic absorption spectroscopy (FAAS) method as recommended by United State Environmental Protection agency (USEPA) [27]. The results are presented as average of the determination of triplicate recording of the three sample solutions for each water samples (n = 9). The results are given in Table 7. Chromium and cadmium were below the detection limits in all samples and are reported as not detected (ND). Iron and zinc are found at part per million levels and are reported as mg/L. Comparison of the concentration of each element among the water samples is shown in Fig. 4. Iron and zinc concentration levels are higher in tap water than all other mineral water samples.

Cadmium. Cadmium was found to be below instrument detection limit in all the water samples, which is within the WHO guideline for drinking water 0.003 mg/L. Hence, Cd does not pose any health problem if people drink Ambo, Highland and Aquaddis mineral water. Acute cadmium poisoning symptoms are similar to those of food poisoning. It is associated with cause of kidney disease and linked to hypertension. There is also some evidence that cadmium can cause mutations. The cadmium concentration in unpolluted waters is usually below 0.001 mg/L [22]. 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, and water coolers.

Chromium: The chromium concentration was also found to be below the instrument detection limit as mentioned above in all water samples, hence this undetected value shows the level of chromium in drinking water is not exceeded the current guideline value of 0.05 mg/L [1]. As a practical measure, 0.05 mg/L, which is considered unlikely to pose significant risks to health, has been retained as the provisional guideline value by WHO until additional information becomes available and chromium is re-examined. Therefore all drinking water samples are suitable for drinking as far as chromium is concerned.

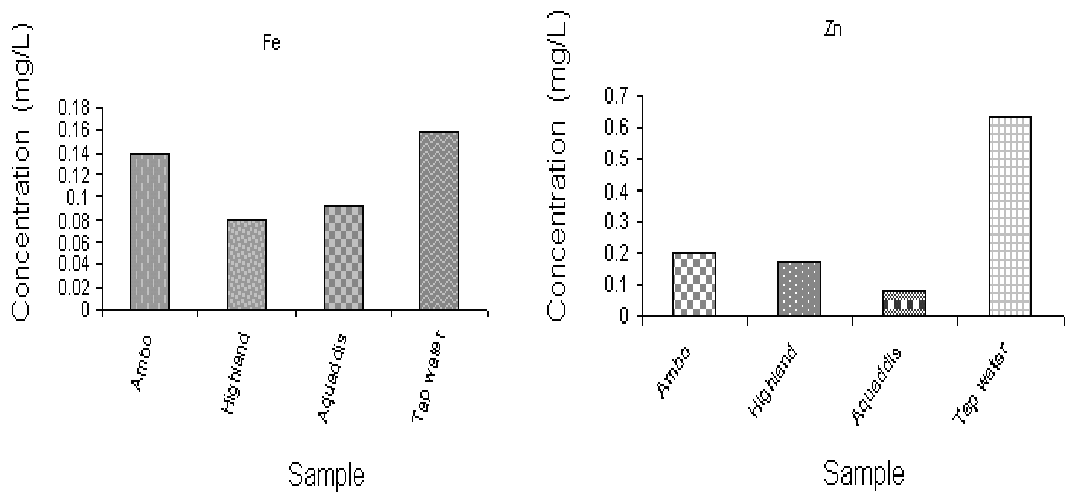
Iron: In contrast to chromium and cadmium, iron was detected appreciably in all the water samples. Iron concentration ranges from 0.079 to 0.16 mg/L. Iron was relatively higher in tap water than in all of bottled mineral water samples that were analyzed (Ambo, Highland and Aquaddis mineral water samples) and Highland has got the lowest value of iron. Ambo mineral water had the highest iron levels among the bottled mineral water with the concentration levels of about 0.14 mg/L. But the amount found in Ambo mineral water sample is less than that of in tap water sample. In mineralized spring water with a total dissolved solid content of 500 mg/L, the taste threshold value was 0.12 mg/L. The level of 2 mg/L of iron was recommended by WHO does not pose a hazard to health. But the taste and appearance of drinking water will usually be affected below this level [1]. Therefore the bottled mineral water samples currently analyzed as well as tap water sample have no any health effect on humans upon drinking these waters as far as iron is concerned.

Zinc: The concentration of zinc in all the water samples was appreciably detected and found larger than all the four other heavy metals analyzed with the concentration ranges between 0.08 - 0.64 mg/L. Zinc was higher in tap water than bottled mineral water but the concentration range in all samples is within the levels recommended for good health, since the levels of zinc in all water samples are much lower than the accepted value of WHO guideline 5 mg/L for drinking water. It is interesting that the filtration of water during water treatment at the source actually increase the level of zinc in tap water possibly due to leaching from materials used in manufacturing the filters and also from the leaching of galvanized pipes in the way water flows through the pipes. According to some report from Egypt [22], zinc imparts an undesirable astringent taste to water. Water containing zinc at concentrations in the range 3-5 mg/L also tends to appear opalescent and develops a greasy film when boiled. Therefore none of the analyzed water samples can show any of the problem mentioned above as the concentration level of zinc in all sample is very low.

Table 7. Average trace metal concentration in the water samples.

Type of sample	Concentration (mean ± SD) of metals (mg/L)			
	Fe	Cr	Cd	Zn
Ambo	0.14 ± 0.012	ND	ND	0.20 ± 0.027
%RSD	8.6	ND	ND	**13.5**
Highland	0.079 ± 0.0045	ND	ND	0.17± 0.0054
%RSD	5.7	ND	ND	3.1
Aquaaddis	0.093 ± 0.005	ND	ND	0.08 ± 0.0079
%RSD	5.4	ND	ND	9.9
Tap water	0.16 ± 0.0053	ND	ND	0.64 ± 0.011
%RSD	3.3	ND	ND	1.7

Note: ND not detected.



(a) (b)

Fig. 4. (a) Average concentration of Fe and (b) average concentration of Zn in the four water samples.

3.3 Determination of Common Ions and Some Physical Parameters

Determination of common cations and anions were 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_2^-, Br^-, SO_4^{2-}, and PO_4^{3-}) using an Anion-Exchange CG17A column and major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) using Cation-Exchange CS12A analytical column that are connected to guard columns was determined and the results of these analysis are summarized in Table 8. During the analysis of four drinking water samples for major cations and an associated anions, Ambo mineral water showed over range for all the analytes mentioned above and Aquaddis also showed an over range signal for sodium. Therefore both of the samples were diluted (Ambo 1:20 factors) and (Aquaddis 1:10 factors). Finally the correct results were obtained. After determination was over the results were calculated by multiplying the results by the dilution factors. The results were reported as the average of the triplicate results (n = 3) of each analyte in all samples.

Table 8. The average concentration of common ions in mg/L and physical parameters in bottled and tap water samples.

Parameters	Concentration/values in the samples (mean ± SD)			
	Ambo	Highland	Aquadiss	Tap water
pH	6.5 ± 0.01	7.94 ± 0.015	8.23 ± 0.01	7.76 ± 0.025
% RSD	0.15	0.19	0.12	0.32
Ec (μS/cm)	1788 ± 5.5	393 ± 1.5	296 ± 1.7	102 ± 0.6
% RSD	0.31	0.38	0.57	0.59
Na^{+}	195± 1.5	18.3 ± 1.5	40.3 ± 2.6	2.02 ± 0.05
% RSD	0.77	8.2	6.5	2.5
K^{+}	21.9 ± 0.91	4.81 ± 0.19	2.82 ± 0.23	1.03 ± 0.03
% RSD	4.2	4.0	8.2	2.9
Mg^{2+}	36.3 ± 4.3	8.21 ± 0.59	1.87 ± 0.1	1.97 ± 0.12
% RSD	**11.8**	7.2	5.2	6.0
Ca^{2+}	51.4 ± 3.3	35.4 ± 0.36	5.41 ± 0.45	9.43 ± 0.04
% RSD	6.4	1.0	8.3	0.42
F^{-}	0.70 ± 0.004	ND	2.25 ± 0.22	ND
% RSD	0.58	ND	9.8	ND
Cl^{-}	48.1 ± 1.9	3.57 ± 0.46	6.67 ± 0.86	3.96 ± 0.34
% RSD	3.9	**12.9**	**12.9**	8.6
Br^{-}	ND	17.4 ± 2.4	ND	5.75 ± 0.63
% RSD	ND	**13.8**	ND	**10.9**
NO_3^{-}	13.9 ± 0.48	2.83 ± 0.12	2.48 ± 0.19	1.86 ± 0.21
% RSD	3.5	4.2	7.7	**11.3**
SO_4^{2-}	ND	2.63 ± 0.33	6.45 ± 0.64	2.31 ± 0.28
% RSD	ND	**12.5**	9.9	**12.1**
PO_4^{3-}	ND	ND	ND	ND
% RSD	ND	ND	ND	ND

Note: ND- not detected.

3.3.1 Determination of Common Inorganic Cations

The majority of the inorganic cations listed as a primary drinking water contaminants by the U.S. Environmental Protection Agency are transition metals which are most commonly analyzed using spectroscopic methods, such as atomic absorption spectroscopy and inductively coupled plasma spectroscopy [27].

Ion chromatography provides a straight forward method for the simultaneous analysis of alkali and alkali earth metal cations in drinking water as described in ISO Method 14911-1 [50]. In this study two alkali metal cations (sodium and potassium) and two alkali earth metal cations (magnesium and calcium) were analyzed in bottled drinking water and tap water samples and the results are discussed below separately for each cations. Figure 5 shows ion chromatogram of alkali and alkali earth metal cations (sodium, potassium, calcium and magnesium) that obtained using Dx-600 Dionex Ion chromatography in the four drinking water samples.

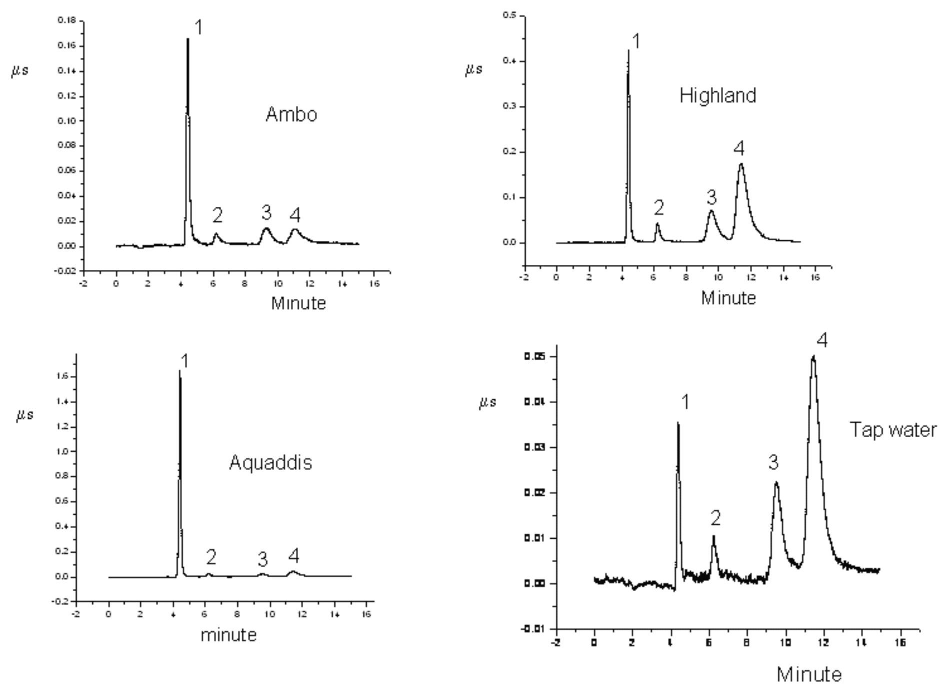


Fig. 5. Chromatogram of cations in drinking water samples: 1-sodium, 2-potasium, 3-magnesium, 4-calcium.

This study confirmed that the concentration of common metals ions (Na^{+}, Mg^{2+}, K^{+} and Ca^{2+}) in bottled mineral waters varies with the type of sample analyzed. This may be due to the fact that the origin of these water samples is different, as they are from different sources. The highest concentrations of these metals were determined in Ambo mineral water than the rest of other mineral water samples currently analyzed (Highland, Aquaddis). When it is compared to the content of tap water sample, the concentration of these cations in all the mineral water is higher than that in tap water except calcium, which is higher in tap water than Aquaddis mineral water and this is verified in Figure 6. The average concentration of triplicate (n = 3) of these metals in drinking water sample is compared.

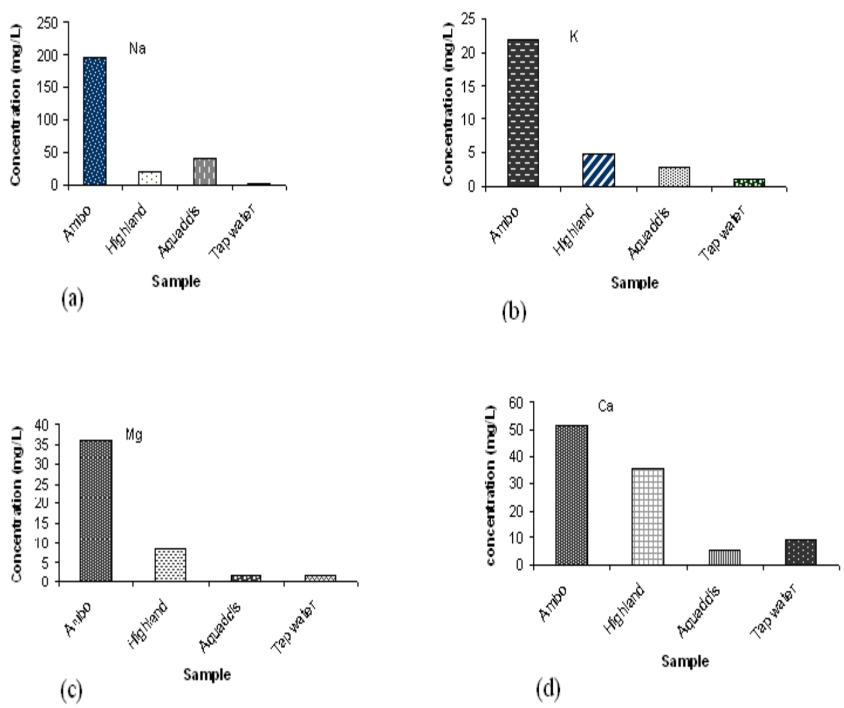


Fig. 6. (a) Sodium, (b) potassium, (c) magnesium (d) calcium average concentrations in bottled mineral water and tap water samples.

Sodium and potassium: Both are very important for human body and regulate the water balance and the acid-base balance in the blood and tissue. The major intracellular cation is potassium with the average concentration of 140 mg/L. The extra cellular potassium concentration, though very important and tightly regulated much lower, at 3.5-5 mg/L.

The major extracellular cation is sodium with an average concentration of 140 mg/L. Intracellular sodium concentration is much lower at about 12 mg/L. These differences are maintained by the Na^+, K^+ -ATPase ion pump located in the cell membrane of virtually all cells. Sodium and potassium both are essential nutrients and the Food and National Board of the National Research Council of America recommends that sodium intake be limited to no more than 2400 mg per day. The Committee on Dietary Allowances recommends 1875 – 5625 mg per day of potassium in order to maintain adequate and safe levels of potassium balance [51].

Sodium: Sodium in drinking water is not a health concern for most people because in health people, excess sodium is eliminated through the kidneys and the correct balance of sodium and water is maintained. But for people with heart disease, hypertension, kidney disease and circulatory illness, it may be an issue of health concern because of their inability to maintain the required body balance of sodium [23, 51]. The WHO and USEPA have restricted people with hypertension or those on sodium-restricted diet to drink water with sodium content not more than 20 mg/L and those on moderate restricted diet should not drink water containing more than 270 mg/L of sodium [23].

In this study the average concentration of sodium is compared in each water sample as shown in Figure 6a. The maximum amount is determined in Ambo mineral water and the lowest is in tap water sample. The concentration ranges from 2.02 in tap water to 195 mg/L in Ambo water**.** Among these four drinking water samples, highland mineral water and tap water samples are suitable for both people with the stated health problems. Ambo and Aquaddis mineral waters are not suitable for people with hypertension or sodium restricted diet but it is suitable for moderately restricted sodium diet. According to WHO guidelines for maximum concentration level of sodium in drinking water, only Ambo bottled water exceeded that recommendation with a value of 160 mg/L. Sodium may affect the taste of drinking water at level above 200 mg/L [1]. Therefore according to this study people with hypertension health problem are advised to drink Highland in preference to Ambo and Aquaddis mineral waters. Even it is better for these people to drink tap water than that of Ambo and Aquaddis concerning the level of sodium in these water samples.

Potassium: There is no fixed health guidelines for the amount of potassium present in water that would be considered safe by the WHO. Drinking water is not the major dietary source of potassium, and the concentration in drinking water seldom reaches 10 mg/L. However, USEPA has set a maximum level of 100 mg/L. In people on low potassium diets, strokes, high blood pressure, and diabetes occur more frequently than in those who consume sufficient or high potassium diets [1]. The potassium content of drinking water varies greatly depending on its source. It tends to be larger in mineral waters than ordinary tap water.

In this study in the same way to that of sodium the average concentration of potassium in mineral water sample are compared as shown in Figure 6b and it is found to be higher in mineral water samples than that in tap water. The highest value is in Ambo mineral water and the lowest is in tap water, ranging from 21.9 to 1.03 mg/L. Since getting adequate potassium in the diet is hampered by the relative few good sources of potassium and further by their limited consumption, potassium in the water represents a potentially significant benefit to the majority of people. Considering this view, brands containing no or very low potassium are also not beneficial for human health. Out of the three brands, two of them (Highland and Aquaddis) had potassium content less than 5 mg/L. Tap water sample had potassium even less than 1.5 mg/L. So the people suffering from high blood pressure and relying upon only these bottled drinking water are liable to aggravate their symptoms as all of the bottled water samples are lacking in potassium. Even relying on only tap water has also more problem as it contains less amount of potassium than bottled water samples.

Calcium and Magnesium: The WHO limits hardness for drinking water between 100 – 500 mg/L. Hardness of water which is due to the presence of calcium and magnesium salts in water, does contribute towards total calcium and magnesium human dietary needs, which has a beneficial effect on bone structure. Studies on water hardness and cardiovascular disease mortality have suggested a lower incidence of heart disease in communities drinking hard water. Extremely hard water (hardness > 500 mg/L) is also unfit for consumption because the constituent minerals such as calcium can deposit inside the body if present in high amounts leading to kidney or gall bladder stones. Consumption of very soft water (hardness < 50 mg/L) lacking in essential minerals like calcium, magnesium and other trace minerals is also harmful for the body because water low in mineral content would rob off the body's minerals. People drinking such treated water excrete huge amounts of calcium, magnesium and other trace minerals in urine. The more the mineral loss, the greater the risk for osteoporosis, osteoarthritis, hypothyroidism, coronary artery disease, high blood pressure and a long list of degenerative disease generally associated with premature aging [51].

Magnesium: There is a significance difference in magnesium concentrations between mineral water analyzed in this study and tap water sample except Aquaddis which shows relatively similar content of magnesium to that of tap water. Ambo and Highland have got higher concentration of magnesium as compared to tap water. The two brands Highland and Aquaddis had magnesium concentration less than the respective lower limit of 30 mg/L as prescribed by the WHO. Thus these bottled water samples violate the lower limit of the WHO for magnesium; hence it leads to the health problem due to magnesium deficiency, provided that humans rely only on these mineral water for drinking. But Ambo mineral water is in the limit that prescribed by WHO for magnesium that it is suitable for drinking if people in need of magnesium. The concentration of magnesium ranges from 1.87 in Aquaddis to 36.3 mg/L in Ambo bottled water. This is summarized in Figure 6c.

Calcium: All the water samples currently analyzed had calcium less than the respective lower limit of 75 mg/L as prescribed by the WHO. The relative concentration of calcium is higher in Ambo bottled water than in all other samples currently analyzed. Aquaddis showed very low levels of calcium as compared to all the rest, as shown in Figure 6d and the concentration of calcium ranges from 5.41 in Aquaddis to 51.4 mg/L in Ambo water.

Drinking frequently only these bottled water leads to encounter with the above mentioned health problems. Natural water sources typically contained concentrations up to 10 mg/L calcium. However, concentrations up to 100 mg/L are fairly common in natural sources of water. The taste threshold for calcium ion is in the range 100-300 mg/L, depending on the associated anions but higher concentrations are acceptable to consumers. Hardness levels above 500 mg/L are generally considered to be aesthetically unacceptable. Calcium is one of the major elements responsible for water hardness. Water containing less than 60 mg/L of Ca is considered as soft water [1, 51]. Therefore none of the samples (Ambo, Highland Aquaddis and tap water) currently analyzed are considered as hard water rather it in the category of soft water according to the above information.

3.3.2 Determination of Common Inorganic Anions

The U.S. National Primary Drinking Water Standards specify a maximum contaminant level (MCL) for a number of inorganic anions including fluoride, nitrate and nitrite [52]. The MCLs are specified to minimize potential health effects arising from the ingestion of these anions in drinking water. Consequently the analysis of these anions in drinking water samples is mandatory. Other common anions such as chloride and sulfate are considered secondary contaminants. The secondary standards are guidelines regarding to taste, color, odor and certain aesthetic effects.

Ion chromatography has been approved for compliance monitoring of these common inorganic anions in drinking water as described in EPA method 300.0 [21]. This method specifies the use of Dionex IonpacCG17 anion exchange column with eluent of 20 mM KOH for the separation of common anions. Figure 7 shows a chromatogram of common anions in drinking water samples obtained using IonpacCG17 analytical column.

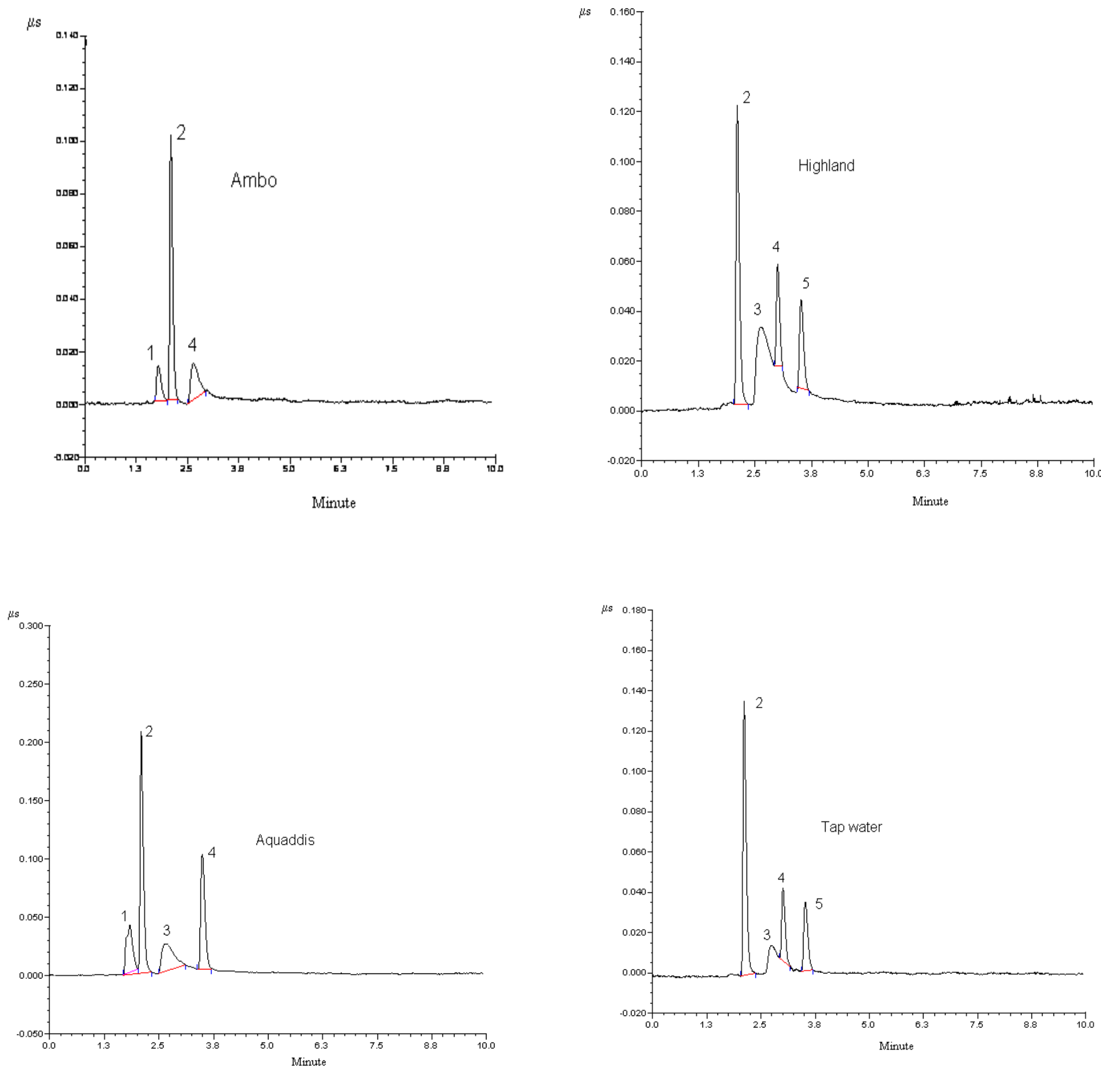


Fig. 7. Chromatogram of anions in drinking water: 1-fluoride, 2-chloride, 3-bromide, 4-nitrate, 5-sulfate.

In this study the common anions including fluoride, chloride, bromide, nitrate, sulfate and phosphate were analyzed in bottled mineral water and tap water samples to investigate the health effects of these anions in drinking water consumed in Addis Ababa. The results are summarized in Table 8 and Figure 8. All samples analyzed had no phosphate at all. The rest of the analytes are discussed separately.

Fluoride: Fluoride is recognized as having a benefit effect on the development of children’s teeth with 1.0 mg/L being the optimum concentration. Fluoride supplements are recommended for children between 3 and 13 years age if the level of fluoride in drinking water is below 0.3 mg/L [51]. However, concentration over 1.5 mg/L may damage children's teeth causing staining, mottling or cavities, the condition known as dental fluorosis.

Out of the three bottled mineral water samples analyzed, one had fluoride level above the upper limit of fluoride sited by WHO (1.5 mg/L) [1]. Aquaddis contained about 2.25 mg/L fluoride, Ambo mineral water has got about 0.7 mg/L, and Highland had no fluoride content at all. Thus, those people, especially children, consuming only Aquaddis bottled mineral water can face the problem of dental fluorosis, and those people especially children consuming only Highland mineral water for drinking purposes are advised to supplement their fluoride intake, may be by the use of fluorinated toothpastes. Tap water contains no fluoride concentration, the comparison of the concentration of fluoride in bottled mineral water and tap water samples are summarized in Figure 8a. The concentration of fluoride is very much higher in Aquaddis mineral water than Ambo mineral water sample and there is no concentration of fluoride in Highland and tap water. No need of comparing the results obtained in this method with the labeled value as there was no fluoride concentration label on all of the bottled mineral water samples. Some research in Italy, on the chemometric survey of Italian bottled mineral water showed that out of 132 brands of bottled water samples, the fluoride concentration in some brands were above the WHO recommended limits of fluoride and in some brands even reaches about 8.4 mg/L [53]. This confirms that the high amount of fluoride concentration obtained in Aquaddis bottled mineral water samples will be possible results.

Chloride: Chloride content of the three brands was range from 3.57 in Highland to 48.1 mg/L in Ambo mineral water, where as the WHO prescribed limit of 250 mg/L in drinking water. Thus all the bottled water samples were safe for drinking from the chloride point of view. If we compare the chloride concentration level in bottled mineral water to that in tap water sample, all bottled mineral water contain higher chloride concentration than tap water except Highland bottled mineral water. The comparison of this analyte in each sample is given in Figure 8b.

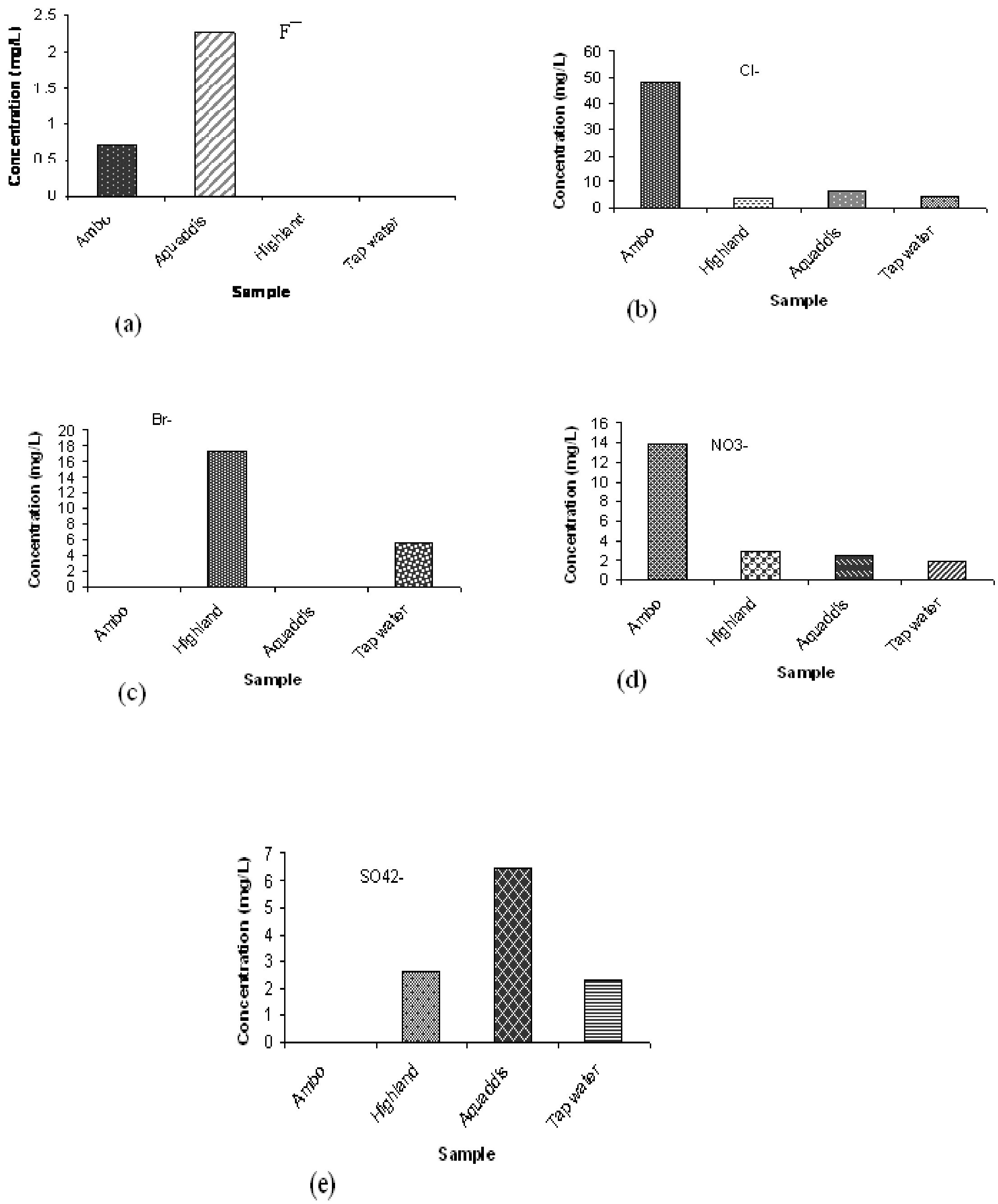


Fig. 8. Average concentration of (a) fluoride, (b) chloride, (c) bromide, (d) nitrate, and (e) sulfate in bottled mineral water and tap water samples.

Bromide: Bromide was not detected in Ambo and Aquaddis bottled mineral water samples, but higher amount was determined in Highland bottled mineral water in the range of 17.4 mg/L. Bromide was also detected in tap water sample; however, the amount in tap water was much lower than in Highland bottled mineral water, this is shown in Figure 8c. Bromide was not claimed by all the companies on the bottles of the mineral water samples.

Nitrate: None of the water samples that were analyzed showed any significant level of nitrate ions except Ambo which had high level of nitrate about 13.9 mg/L. However this value of nitrate in Ambo mineral water is well below the WHO recommended limit of 50 mg/L, and hence does not pose much health concern. When compared to municipal tap water the nitrate content of all bottled mineral water samples are higher and shown in Figure 8d. Nitrate was not labeled on all of the bottled mineral water samples. But it was detected in all samples in this study.

Sulfate: Sulfate is not detected in Ambo mineral water. Relatively significant amount of sulfate concentration was detected in Aquaddis mineral water. The concentration of sulfate in tap water is lower than both in Aquaddis and in Highland mineral water (Figure 8e). Sulfate is labeled only on Ambo mineral water as 0.77 mg/L, but it was detected in all bottled mineral water samples except in Ambo. The amount detected in Aquaddis was 6.45 mg/L and in Highland 2.63 mg/L. This shows non-uniformity in the labeling of the composition of mineral waters which again leads to lack of transparency to the consumers.

Sulfate is one of the least toxic anions. The lethal doses for human as potassium or zinc sulfate are 45 g. The major physiological effects resulting from the ingestion of large quantities of sulfate are catharsis, dehydration, and gastrointestinal irritation. No health-based guideline value for sulfate in drinking water is proposed by WHO. However, because of the gastrointestinal effects resulting from the ingestion of drinking water containing high sulfate levels, it is recommended that health authorities be notified of sources of drinking water that contain sulfate concentration in excess of 500 mg/L [1].

Phosphate: No phosphate was detected in all the bottled drinking water and tap water samples. Like sulfate, phosphate was also labeled only on Ambo bottled mineral water as 0.06 mg/L.

3.3.3 Determination of Physical Parameters

pH: pH has no direct adverse effect on human health, however, according to WHO guidelines, the maximum desirable limit of pH is 7.0-8.5, and USEPA established pH limits from 6.5-8.5 [51]. Waters with pH lower than 4 have a sour taste and above 8.5 an alkaline bitter taste. High pH induces the formation of trihalomethanes, which are toxic. pH below 6.5 starts corrosion in pipes, thereby releasing toxic metals such as Zn, Pb, Cd, Cu, etc. Out of the four types samples analyzed, the three samples (Highland, Aquaddis and tap water) had pH value between 7.0 and 8.5. Ambo bottled mineral water had pH value below 7, which was just slightly acidic with pH value 6.5 and it was out of the range of pH given by WHO guideline, but all the samples analyzed had pH within the prescribed limits recommended by USEPA guideline. The range of pH values in currently analyzed drinking water samples is between 6.5 in Ambo and 8.23 in Aquaddiss. The results of pH value of each sample are given in Table 8. Therefore according to the USEPA guidelines all the bottled as well as the tap water samples are suitable for drinking. When it is compared to the value claimed by the companies, Highland has got no significant pH difference as compared to the labeled value, 7.5 pH as labeled value, 7.9 pH as determined value. But in Aquaddis there is a significant difference between labeled value and the determined one, 6.7 as labeled value, 8.23 as determined value. Ambo bottled mineral water has no labeled pH value at all.

Electric Conductance (EC): Conductivity is a measure of the ability of aqueous solution to carry an electric current that depends on the presence and total concentrations of ions, their mobility and valance [54]. The EC is a valuable measure of the amount of cations and anions in water. In this study, its value ranges in the bottled mineral water from 296 in Aquaddis to 1788 μS/cm in Ambo bottled mineral water. All bottled mineral waters have got higher conductivity than tap water which has conductivity of 102 μS/cm**.** From conductivity values of each water sample, Ambo bottled mineral water contains higher minerals than the rest of bottled mineral water as well as tap water samples.

3.4 Comparison of current results with the labeled values

The current results were compared with that of claimed value using t- test and the results are discussed in Table 9. t-test is usually used to compare weather there is any significant difference between the true mean and the measured mean values of a given analytical data. 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^{2+}, Ca^{2+} and Cl^- are labeled in all the three brands (Ambo, Highland and Aquaddis) of mineral waters consumed in Addis Ababa. 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 are significant difference between the labeled values and the results obtained in this study for all compared analytes except Mg^{2+} in Ambo and Aquaddis and Cl^- in Aquaddis.

Table 9. Comparison of analytes on the labels with current results in mg/L.

Analyte	Sample								
	Ambo			Highland			Aquaddis		
	Label	Current R.	t-value	Label	Current R.	t-value	Label	Current R.	t-value
Na^+	252	195 ±1.5	65.8	26	18.3±1.5	8.9	23.8	40.3±2.6	11.0
K^+	35	21.9±0.91	24.9	7	4.8±0.19	20.0	1.65	2.82±0.23	15.3
Mg^{2+}	46	36.3±4.3	**3.9**	13	8.2±0.59	24.4	1.95	1.87±0.1	**1.4**
Ca^{2+}	72	51.4±3.3	10.8	41	35.4±0.36	26.9	3.2	5.4±0.45	14.7
Cl^-	32.5	48.1±1.9	14.2	5	3.6±0.46	6.7	7.6	6.67±0.86	**3.2**

3.5 Analysis of Variation in Composition of Bottled Mineral Water Samples Currently Analyzed

To know weather the composition of the samples of mineral water are significantly different or not it is important to use the application of analysis of variance (ANOVA). ANOVA is an extremely powerfully statistical technique which can be used to separate and estimate the different causes of variation. The calculation of one–way ANOVA for practical purposes was done on computer using both Minitab and Excel software [55]. In this study Minitab software was used to calculate the ANOVA for testing the significant differences in the composition of Ambo, Highland and Aquaddis mineral water. According to Minitab, 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 Zn concentration in Ambo and Highland, Fe concentration in Ambo and Aquaddis and Fe in Highland and Aquaddis. The F-value and P-value are given in Table 9.

Table 10. Degree of freedom (DF), F-values and P-values at 95% confidence level.

Parameters	Comparison								
	Ambo and Highland			Ambo and Aquaddis			Highland and Aquaddis		
	DF	F-value	P-value	DF	F-value	P-value	DF	F-value	P-value
pH	5	40,000	0.000	5	67,000	0.000	5	739.60	0.000
EC	5	70,000	0.000	5	200,000	0.000	5	5148.06	0.000
Na^+	5	8891.35	0.000	5	8267.27	0.000	5	164.13	0.000
K^+	5	394.49	0.000	5	1072.63	0.000	5	53.42	0.002
Mg^{2+}	5	48.86	0.005	5	197.08	0.000	5	335.09	0.000
Ca^{2+}	5	25.77	0.013	5	565.98	0.000	5	8000.40	0.000
F^-	5	82.10	0.002	5	116.43	0.000	5	311.36	0.000

Cl^-	5	614.23	0.000	5	1192.55	0.000	5	30.54	0.005
Br^-	5	18.28	0.021	5	-	-	5	47.86	0.002
NO_3^-	5	2434.97	0.000	5	4690.85	0.000	5	1.72	0.260
SO_4^{2-}	5	30.06	0.010	5	361.79	0.000	5	73.24	0.001
Fe	5	26.01	0.013	5	0.70	**0.450**	5	1.07	**0.359**
Zn	5	0.14	**0.877**	5	10.30	0.033	5	22.21	0.009

3.6 Comparison of Current 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 mineral water 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 [23]. These countries include Egypt, Australia, Belgium, Canada, China, France, Germany, Hong Kong, Iceland, Indonesia, Italy, Japan, Malaysia, Portugal, Scotland, Sweden, Thailand, Turkey, United Kingdom and USA. From each country the number of brands reported was as follows. Egypt, five brands (Safi, Mineral, Baraka, Delta and Siwa); Australia, six brands (A_1, A_2, A_3, A_4, A_5, and A_6); Canada, two brands (Ca_1 and Ca_2); China, eight brands (C_1, C_2, C_3, C_4, C_5, C_6, C_7 and C_8); France, eight brands (F_1, F_2, F_3, F_4, F_5, F_6, F_7 and F_8); Germany, only one brand (G_1); Hong Kong, five brands (A, B, C, D and E)); Iceland, only one brand (Ic_1); Indonesia, six brands (I_1, I_2, I_3, I_4, I_5 and I_6); Italy, three brands (It_1, It_2 and It_3); Japan, three brands (J_1, J_2 and J_3); Malaysia, three brands (M_1, M_2 and M_3); Portugal, two brands (P_1 and P_2); Scotland, two brands ($Sc_1$and Sc_2); Sweden, only one brand (Sw_1); Thailand, two brands (T_1 and T_2),; Turkey, only one brand (Tu_1); UK, four brands (Uk_1, Uk_2, Uk_3 and Uk_4) and USA, two brands (U_1 and U_2). The reports show that, all mineral water samples were analyzed for common ions (F^-, Cl^-, NO_2^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}). The comparison of current study was done with these reported results as range of the results of all brands for each ion as given in Table 10. In this study three brands were analyzed (Ambo, Highland and Aquaddis) for heavy metals and common ions. Except some outlined results the composition of the bottled mineral water samples from different countries show more or less similar composition. These outlined results are shown by bolding the results.

Table 11. Comparison of the results obtained by current study with results from other countries in mg/L of analytes [23].

Country	Analytes							
	F^-	Cl^-	NO_2^-	SO_4^{2-}	Na^+	Mg^{2+}	K^+	Ca^{2+}
Ethiopia	0.0-**2.25**	3.57 - 48.1	2.5 - 13.9	0.0 - 6.45	18.3- **195.4**	2.82 - 21.9	1.87- **36.3**	5.41-51.4
Egypt	0.12 - 0.48	11.1- **221.1**	0.1 - 18.7	10.4 - 68.12	4.49 - **169**	1.54 - 23.3	0.11-18.5	1.39-44.8
Australia	0.10 - 0.22	5.9 - 47.4	0.6 - 24.8	0.7 - 6.8	2.4 - 34.5	5.7 - 38.6	0.7-20.0	0.5-4.6
Belgium	0.03 - 0.19	5.7 -11.4	0.2 - 1.3	4.0 - 4.7	7.2 - 7.9	1.2	1.2-1.3	6.0
Canada	0.2 - 0.36	0.0	0.2 - 1.0	1.7 - 6.7	0.0 - 1.5	0.0 - 0.7	0.2-6.0	3.0-7.9
China	0.07 - 0.79	0.0 – 67.0	0.9 - **35.9**	0.5 - **177.0**	8.1 - 31.4	1.0-12.5	0.4-24.1	0.7-**171.4**
France	0.0 - 0.49	4.3 - **125.3**	0.0 - 18.3	7.2 - **1039.0**	7.5 - 49.0	2.2 - 21.0	5.0 - **58.9**	6.5- **468.6**
Germany	0.0	45.8	1.1	47.0	**227.0**	**50.5**	170.5	113.0
Hong Kong	0.0 - 0.44	7.9 - 80.9	0.0 - 4.2	0.0 - 98.7	0.0 - 44.0	0.2 - **47.3**	0.0-6.4	2.4-22.0
Iceland	0.04	15.9	0.7	2.6	14.7	0.0	1.1	4.7
Indonesia	0.0 - 0.31	0.0 - 26.4	0.7 - **38.1**	1.3 - 27.2	9.1 - 40.0	2.8 - 10.3	4.3-70.7	2.8-21.4
Italy	0.0 - 1.2	0.0 - 19.4	5.1 - 9.1	4.8 - 41.5	3.3 - 30.9	0.8 - **48.0**	0.5 - **26.5**	6.3-40.0
Japan	0.0 - 0.02	3.0 - 7.8	0.5 - 1.5	0.4 - 2.3	7.9 - 8.4	0.4 - 2.1	0.9-2.8	0.4-2.1
Malaysia	0.05 - **2.62**	2.9 - 22.9	0.0 - 13.5	0.9 - 3.2	5.8 - 30.8	4.0 - 5.8	0.0-3.4	4.9-18.3
Portugal	0.0 - 0.05	8.6 - 15.8	1.3 - 1.9	0.7 - 1.3	7.6 - 11.8	3.0 - 4.3	1.5-13.6	0.0-22.1
Scotland	0.05 - 0.1	8.6 - **138.6**	1.1 - 4.8	0.8 - 8.0	8.1 - 58.0	2.9 - 3.1	13.3 - 17.9	47.7-**110.0**
Sweden	**2.4**	26.5	0.7	9.3	**225.0**	1.9	0.6	5.5
Thailand	0.03 - 1.81	30.7- **133.2**	0.2 - 0.4	1.7 - 33.9	68.0 - 69.2	15.1 - 25.0	0.2 -14.9	31.6-38.0
Turkey	0.0	0.0	1.7	3.8	0.4	0.1	4.6	31.0
UK	0.0 - 0.1	15.1 - 33.5	0.3 - 15.0	3.6 - 70.0	10.3 - 30.0	0.8 - 5.0	1.4 - **26.0**	54..6-**140.0**
USA	0.0 - 0.25	7.2 - **214.1**	0.4 - 0.6	6.0 - 106.1	0.0 - 11.1	3.8 - 4.3	0.2-3.7	9.1-79.7

3.7 Comparison of Current Results with Some National and International Guidelines

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. Examples of chemical hazards include lead, arsenic fluoride, chromium, cadmium, etc. and microbial hazards, include bacteria, viruses and parasites, such as *Vibrio cholerae*, hepatitis A virus, and *Crytosporidium parvum*, respectively. Physical hazards include glass chips and metal fragments. Because of the large number of possible hazards in drinking-water, the development of standards for drinking-water requires significant resources and expertise, which many countries are unable to afford. Fortunately, guidance is available at the international level. The World Health Organization (WHO) publishes guidelines for drinking-water quality which many countries use as the basis to establish their own national standards. The guidelines represent a scientific assessment of the risks to health from biological and chemical constituents of drinking-water and of the effectiveness of associated control measures. 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 [23].

In this experiment about six 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. These standard guidelines are UK, EC, WHO, USEPA, China limit and Ethiopian limit. The Ethiopian standard was developed on March 2002 for drinking water depending on the WHO guidance and considering the geographical, economical and cultural values of the country [56]. According to these standard guidelines, no analytes are above the given standards except fluoride in Ambo and Aquaddis, which is above the limit of all the standards and sodium and potassium in Ambo also exceed the UK maximum contaminant level. Therefore all the water samples can be used for drinking as it is within the limits of all the guideline.

Table 12. Comparison of current results with some national and international guidelines.

Guidelines	**Species in mg/L**													
	F^-	Cl^-	Br^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe	Cr	Cd	Zn
UK (MCL)	1.5	400	_	50	250	_	150	12	50	250	_	_	_	_
WHO	1.5	250	_	50	250	_	200	_	_	_	0.2	0.005	0.003	5
EC	1.5	250	_	50	250	_	200	_	_	_	0.2	_	_	_
USEPA (1993)	2	250	_	44	250	_	_	_	_	_	_	0.1	0.005	_
China, limit	1	250	_	88	250	_	_	_	_	_	_	_	_	_
Ethiopian, limit	3	533	_	50	450	_	350	_	_	_	0.4	0.1	0.003	6
Ambo	0.70	48.1	ND	13.9	ND	ND	195	21.9	36.3	51.4	0.11	ND	ND	0.20
Highland	ND	3.57	17.4	2.83	2.63	ND	18.3	4.81	8.21	35.4	0.079	ND	ND	0.17
Aquaddis	**2.25**	6.67	ND	2.48	6.45	ND	40.3	2.82	1.87	5.41	0.093	ND	ND	0.08
Tap water	ND	3.96	5.75	1.86	2.31	ND	2.02	1.03	1.97	9.43	0.157	ND	ND	0.64

Note: the «-» indicates the limits are not given.

4. CONCLUSION AND RECOMMENDATION

Water is essential for life and its increasing consumption for drinking as well as the necessity to protect and inform the consumers explains the interest to study its quality. Based on the results of this study, there is a large variation in the bottled mineral water composition among the brands compared, thus the consumer can choose the mineral water according to its preference.

The inorganic composition of a number of mineral water samples from different sources were determined and compared with that of tap water sample. The common cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) concentrations are higher in mineral water than in tap water except calcium in Aquaddis. Among four heavy metals only Fe and Zn were detected in all water samples, tap water contains higher concentration of these elements than bottled mineral water samples. The anion concentrations are varying among the samples however the concentrations of these anions are higher in mineral water samples as compared to tap water. Generally mineral water samples contain higher minerals especially common ions than tap water. This was confirmed by conductivity measurement. It is advisable for people who have a problem of blood pressure, kidney diseases, heart disease, and circulatory illness to drink tap water in preference to mineral water.

The results obtained in this research were compared with some of the national and international guidelines. All the parameters determined were below the guideline limits except fluoride in Aquaddis mineral water samples. This mineral water contains fluoride above the maximum concentration allowed for natural waters by WHO guideline and other standards for drinking water and potassium concentration which exceeds the MCL laid by United Kingdom (UK). The importance of the quality of water for human consumption with regard to health makes it necessary to establish norms to regulate it, including limits for all the parameters that directly affect human health and deteriorate water quality.

The results of this study were also compared with the results of other countries' mineral water in the world. Except some outlined results reported from different countries, the composition of mineral waters in Ethiopia is more or less similar to that of other countries.

Finally further studies should focus on the possibility to verify the origin and the authenticity of Ethiopian mineral waters taking into account of increased number of samples and additional parameters like lead, mercury, arsenic, etc.

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