Level of bromate, fluoride, microbial load in ozone, ozone + nano filter and ozone + UV treated packed water brands in Ethiopia

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This thesis is submitted to the College of Natural and Computational Sciences of Addis Ababa University in Partial Fulfilment of the Requirement for the Degree of Master of Science Food Science and Nutrition.

By

Elsabeth Alimaw

March, 2021

Addis Ababa University

College of Natural and Computational Sciences

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By: Elsabeth Alimaw

Supervisor: Dr. Paulos Getachew

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Declaration

I, the undersigned, declare that this thesis titled “**Level of bromate, fluoride and microbial load in ozone, ozone+ nano technology (nano filter) and ozone+ UV treated packed drinking water brands in Ethiopia**” has been carried out and written by me in the Center for Food Science and Nutrition, Addis Ababa University, Addis Ababa, under the supervision of **Dr. Paulos Getachew**. The information derived from the literature has been duly acknowledged in the text and list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution.

By: Elsabeth Alimaw

Signature: ______________

Approved by Examining Boards

Names	**Signature**
Dr. Paulos Getachew	_________________
(Supervisor)	
_________________________	_________________
(External Examiner)	
_________________________	_________________
(Internal Examiner)	
_________________________	_________________
(Chairman)	

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List of abbreviations and acronyms

BGB	Brillight green broth
BDL	Below detection limit
Cfu	Colony forming unit
CNTs	Carbone nanotubes
CES	Compulsory Ethiopian standard
DBP	Disinfection by product
DOC	Dissolved organic carbon
EC	*Escherichia coli* broth
FO	Ford osmoses
HAA5	Five of the halo acetic acids
HCL	Hydrochloric acid
IARC	International Agency for Research on Cancer
IC	Inorganic carbon
LADD	Lifetime average daily dose
LMW	Low molecular weight
LSB	Luray sulfate broth
MAC	Maximum Admissible Concentration
MCL	Maximum contaminant level
MCLG	Maximum contaminant level goal
MDG	Millennium Development Goal
MF	Micro filtration
MSDS	Material Safety Data Sheets
NF	Nano filtration
NOM	Natural organic matter
NP	Nanoparticles
NW	Nestle Waters International
PCA	Plate count agar
RfD	Reference dose

RO	Reverse osmosis
ROS	Reactive oxygen species
TSI	Triple Sugar Iron Agar
TTHMs	Total tri halo methane’s
UF	Ultra filtration
UNICEF	United Nations International Children’s Emergency Fund
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
NTU	Nephelometric Turbidity Unit
WWDP	United Nations World Water Assessment Programme

Abstract

With the increased demand and consumption of packed water in Ethiopia especially in major cities like Addis Ababa, there has been a growing concern about the quality and safety of the product. The public used to consider that all packed waters produce are safe. One of the safety concerns is the formation of bromate as disinfection by-products (DBPs) resulting from ozone treatment. Bromate has been identified as a possible human carcinogen and the level in drinking water should be strictly controlled below 10 μg/L. As an alternative, UV disinfection produces minimal DBPs. However, this technology also requires high dosage for the effective removal of certain viruses. Therefore, the drawback of conventional disinfectants urges the development of alternative approaches that can improve the robustness of pathogenic removal while avoiding the formation of DBP. Thus, the development of nanotechnology, its application in water and wastewater treatment is becoming increasingly popular. But the microbial safety and quality of water upon this treatment in Ethiopia is not investigated as to our knowledge. Furthermore, in most of the bottled water brands the fluoride level, which is vital for the consumer, is not labeled as well. Therefore, the objective of this study was to investigate the level of bromate, fluoride and microbial load in ozone, ozone+ nano filter and ozone + UV treated packed drinking water brands in Ethiopia. For this purpose, thirty samples representing different brands of packed waters were randomly collected from different supermarkets, kiosks, groceries, cafes and distributer cars. The parameters investigated were bromate, fluoride, pH, Electrical conductivity (EC), Total dissolve solid (TDS), Total hardness (TH), alkalinity, turbidity and microbiological; plate count agar (PCA) and total coliform count. It was found that the concentrations of the bromate were quite different from brand to brand even upon the same treatment and water type. The level of bromate in 8 brand packed water was higher than the permissible limit. The fluoride level except ten (33.3%) brands of packed water all are not mentioned on the label of the bottle (packaged).Therefore 66.6% of the sample has not information about fluoride content. The other parameters (PH ,Electrical conductivity, total dissolved solid, total hardness, total alkalinity and turbidity) were fulfills the requirement as per the CES and WHO guide lines and at $p<0.05$.But in some brands the concentrations are far below the requirement and are not recommended for drinking as per WHO standards like PH and total hardness value. All water samples were found free of the microbial contamination.

Keyword: *Ozone treatment, Nano filter, Bromate, Fluoride, Microbial load*

1. INTRODUCTION

1.1. Background

Water is one of the most important and universal molecules on the surface of our planet and in living organisms. It has very specific properties which are responsible for its very broad utilization in nature and our daily life. It is used as a drink directly, after processing and within foods. Among the different drinking water sources, bottled drinking water is safe and potable. Thus, it is currently widely used with an increasing trend in the future also (Cochrane *et al.*, 2006).

In Ethiopia there are more than 70 bottled water manufacturers. These manufacturers commonly use municipal water or deep wheel ground water as a source. Apparently, these water sources have a chance of being contaminated with physical, chemical and microbial hazards. Therefore, to reduce the hazards to acceptable level, different processing methods should be applied. There are a lot of technologies to treat drinking water to make it safe from physical, microbial and chemical hazards. These include sand filter, activated carbon, ultra-filter, Nano filter, reverse osmosis (RO), UV, chlorine (calcium hypo chlorate) and ozone (Goh and Ismail, 2013).

Among which, Ozone (O_3) is widely used in drinking water treatment as disinfectant and oxidant. It is an excellent disinfectant and can even be used to inactivate microorganisms such as protozoa which are very resistant to conventional disinfectants (Von Gunten, 2003). Thus; ozone is becoming increasingly popular in water treatment reducing bacteria, viruses, and protozoans within a short reaction time. Also, it is effective in eliminating unwanted coloration, taste and odor problems in drinking water (wang *et al.,* 2014). However, oxidative water treatment can lead to the formation of disinfection byproducts (DBPs) that have human or environmental health concerns. With this regard, ozonation of natural water in the presence of organic compounds and significant bromide levels can cause the formation of harmful brominated organics and bromate ions (Garcia-Villanova *et al.,* 2010 and 2014).

Bromate is the most potent carcinogen among the regulated DBPs and it is considered as possible human carcinogen (Group 2B) by some organizations (WHO, USEPA) (Parrino *et al.*, 2014). Its ability to produce oxidative stress, resulting in damage to DNA, may play a role in its ability to induce renal tumors (Richardson *et al.*, 2007).

Disinfection process is the last and most important step in water and wastewater treatment process (Hossain *et al.,* 2014). However, the use of conventional disinfectants (i.e., ozone and chlorine as the disinfectant) poses the aforementioned formation of toxic disinfection by-products (Bethi *et al.*, 2016). As an alternative, UV disinfection produces minimal DBPs (Peldszus *et al*., 2004). However, this technology also requires high dosage for the effective removal of certain viruses such as adenoviruses. Therefore, the drawback of conventional disinfectants urges the development of alternative approaches that can improve the robustness of pathogenic removal while avoiding the formation of DBP (Qu *et al.,* 2013).

Thus with the development of nanotechnology, its application in water and wastewater treatment is becoming increasingly popular (Kunduru *et al.*, 2017, Bethi *et al.*, 2016; Zhang *et al.*, 2016). Nanotechnology holds great potential in advancing water and wastewater treatment to improve treatment efficiency as well as to augment water supply through safe use of unconventional water sources (Jun *et al*., 2018). Nano materials are very small in size, i.e., approximately 1–100 nm, and shows unique characteristic that enables them to be used in innovative applications (Peltier *et al*.,2003;Qu *et al.*, 2013; Werkneh *et al.*, 2018) such as in the area of wastewater treatment and others. They exhibit high surface area-to-volume ratio, which is very significant to produce “highly reactive surface area than the bulk counterparts” (Bethi and Sonawane, 2018). Nano-oxides (silver, gold, iron, and titanium) are common Nano materials which have been employed so far for the remediation of pollutants in contaminated water and soil environments (Bethi and Sonawane, 2018, Poulose *et al.*, 2014, Aditya *et al.*, 2013, Rai *et al.*, 2009, Chopra, 2007, Panáček *et al.*, 2006).

But in nanotechnology water treatment disinfectant should possess the following requirements : (i) no formation of harmful disinfectant by-products; (ii) disinfection within a short time; (iii) formation of a broad antimicrobial spectrum; (iv) easy operation and low energy cost; (v) low toxicity to the environment and health of living organisms; (vi) must not to be corrosive and easy to store; and (vi) the sludge after treatment should be safe for final disposal (Bethi *et al.*, 2016; Zhang *et al.*, 2016). Recently, various nanomaterial’s have lower propensity to form DBPs, while they exhibit the antimicrobial characteristics without strong oxidation process. These include

Nano-silver (Rai *et al.*, 2009), chitosan nanoparticles (Higazy *et al.*, 2010), photo catalytic titanium dioxide, TiO_2 (Hebeish *et al.*, 2013), and carbon-based nanomaterials (Martynková and Valášková, 2014).

However in Ethiopia many bottled water manufacturers have not used Nano technology. But some company's used Nano filtration membranes. Nano Filter membranes are widely used in water treatment for drinking water or wastewater treatment. It is a low pressure membrane process that separates materials in the 0.001-0.1 micrometer size. NF membranes are pressure-driven membranes with properties between those of reverse osmosis and ultra-filtration membranes and have pore sizes between 0.2 and 4.0 nm. NF membranes have been shown to remove turbidity, microorganisms (all cysts, bacteria, viruses, and humic materials) and inorganic ions such as Ca^{++} and Na^{+}. It also provides excellent protection from DBP formation if the disinfectant residual is added after the membrane filtration step (Ermias Kiros G/Mariam, 2018).

In addition to safety concern, bottled water is preferred to tap water for reasons such as reduced levels of chlorine and fluoride. The presence of fluoride at elevated concentrations in drinking water can cause severe health effects in humans (Ghaderpoori *et al.*,2009;Bhatnagar *et al.*, 2011; Shen and Schäfer, 2015). The primary route of fluoride ingestion is through drinking contaminated groundwater (Singh and Mukherjee, 2015; Singh *et al.*, 2013; Rao *et al.*, 2013). If such water sources are used for bottled water processing, apparently it will lead to high accumulation in the final product. Exceeded level of fluoride will adversely affect dental health (enamel fluorosis). Similarly, with too low concentration of fluoride, optimal caries prevention will not be achieved (Cochrane *et al.*, 2006). Accordingly, WHO maximum recommended limit of fluoride concentration was 1.5 mg/L.

In Ethiopia, bottled water manufacturing sector is increasing; in which most of the factories apply ozone treatment as disinfectant. However, most of these manufacturers don't put the level of bromate and fluoride in the physicochemical labels on the bottle. New emerging water companies are applying nanotechnology as mitigation to the side effects of oxidative treatment. Yet, as to our knowledge, there are no studies conducted to investigate the levels of bromate and fluoride in the widely sold bottled water brands in the country. Therefore, this study evaluated bromate and fluoride level in different bottled water brands in the country manufactured through ozone, ozone+ nano filter and ozone+ UV treatment. Also, the study investigated the effectiveness of the treatments in reducing/eliminating microbial loads.

1.2. Statement of the Problem

In modern life, carcinogenic diseases are most critical than infectious diseases endangering human life. The major routes of exposure to carcinogens are through food. One of these carcinogens is bromate, which is potentially formed during ozone treatment of packed water. Its ability to produce oxidative stress, resulting in damage to DNA, may play a role in its ability to induce renal tumors (Richardson *et al.*, 2007). Several reports of bromate-induced cancer in experimental animals are available. The clearest evidence comes from studies in F344 rats (DeAngelo *et al*., 1998, Kurokawa *et al*., 1983, 1986a, b, 1987).) The weight of evidence from the rat bioassays clearly indicated that bromate has the potential to be a human carcinogen. Bromate is a carcinogen affecting mainly kidney (WHO, 2005). In health perspective, chronic diseases like cancer are critical nowadays in Ethiopia as well as in the world. However, no one gives values for the toxic effects of drinking water disinfection by products. In general, the statement of the problem can be formulated as lack of information on packed brand water disinfection by products in Ethiopia.

Despite this fact, branded packed water products are widely consumed with lack of sufficient information on the disinfection by products. Yet, as to our knowledge bromate concentration is not indicated in any of the packed water brands in the market. Similarly, if fluoride concentration is not regulated in drinking water as per the allowed standard, it will lead to fluorosis. Also, very few water companies put the concentration of fluoride in the labels. Water is consumed in large amount on daily basis. This study was therefore undertaken to assess the level of bromate in packed brand water products in Ethiopia with three different treatments (ozone, UV, and nano filter).The study also assessed the level of fluoride, Physico-chemicals and microbial load of the packed water brands.

1.3. Objectives

1.3.1. General Objective

To assess bromate concentrations, level of fluoride and microbial load in drinking packed brand water produced in Ethiopia through ozone, ozone +Nano filter and ozone +UV treatments.

1.3.2. Specific Objectives

- To evaluate the level of bromate in ozone, ozone +Nano filter and ozone +UV treated drinking packed brand water produced in Ethiopia.
- To evaluate the level of fluoride in drinking packed brand water produced in Ethiopia.
- To investigate efficiency of ozone, ozone +Nano filter and ozone +UV treatments in reducing/eliminating total viable bacteria and total coliform in bottled water produced in Ethiopia.
- To evaluate physico-chemical parameters like TDS, total alkalinity, pH, electrical conductivity, total hardness and turbidity.

2. LITRATURE REVIEW

2.1. Water

Water is the most important natural resources that are essential to the survival of all organisms (Dizman *et al.*, 2017; FarajiGhasemi *et al.*, 2016; Hassani *et al.*, 2016). Everyone needs water to survive, especially when up to 60% of the human body is composed of it (Ellie Whitney and Rady Rolfs, 2008). Approximately 75% of the earth's surface is covered by water, but only 1% of that is drinkable (Soechtig, 2009). A high quality water is required for drinking purposes for better health (Gorde *et al.*, 2013). Freshwater is already a limiting resource in many parts of the world.

The safety of drinking water might be affected by various contaminants which include chemical, physical and microbiological which can cause serious health problems to human (Chaudhry, 2013). Moreover, human beings depend on water for almost every developmental activity. Because of its importance, the pattern of human settlement throughout the history has often been determined by its availability (Gangil *et al.*, 2013). Most of the diseases in developing countries are caused by drinking of contaminated water. The people living in developing countries lack access to clean water due to environmental pollution (Cobbina *et al.*, 2015). The chemical contaminants in potable water include: some heavy metals, non-metals, disinfection byproducts, nitrate, nitrite, pesticides, and sulfate (Bolawa *et al.*, 2017).

2.2. Packaged drinking-water

Drinking water is considered the most basic needs for ongoing daily consumption to human. (Semerjian, 2011) has defined bottled water as "water that is intended for human consumption and that is sealed in bottles or other containers with no added ingredients except that it may optionally contain safe and suitable antimicrobial agents (Semerjian, 2011). The estimated individual needs of drinking water is about 2 liters per day for people weighed 60 kg and one liter per day for children weighed 10 kg, depending on the nature of the climate and physical activity and the culture of the community (Fewtrell *et al* 2001). Bottled water consumption has been growing steadily worldwide during the past three decades (Semerjian, 2011). It is considered as one of the fastest growing and most vital of all the food and beverage factories.

Consumers purchase packed drinking-water for reasons such as taste, convenience or fashion, but safety and potential health benefits are also important considerations (Ikem *et al*., 2002). There are three major types of bottled water can be identified: natural mineral water, spring water and purified water.

1. Natural mineral water: is microbiologically wholesome water, originating in an underground water table or deposit and emerging from a spring tapped at one or more natural or bore exits (Council Directive 80/777/EEC 1980 and European legislation 2009/54/EC Directive). They are different from drinking water because of their spring purity and conservation, for the constant level of minerals (trace elements or other constituents) and, where appropriate, for certain effects they can determine. Food and drug administration (FDA, USA) regulates bottled water as a food and identifies natural mineral waters as water containing not less than 250 parts per million (ppm) total dissolved solids (TDS), coming from a source at one or more bore holes or springs, originating from a geologically and physically protected underground water source (Code of Federal Regulations, Title 21, Part 165 – Beverages; IBWA 2000).

2. **Spring water:** In United Sates, the IBWA understands spring water as “water derived from an underground formation from which water flows naturally to the surface of the earth”. Spring water must be collected only at the spring or through a bore hole tapping the underground formation finding the spring (IBWA, 2000). In Europe, spring water is different from natural mineral water as it must stick to the same standards applicable to drinking water. It doesn’t need to have a constant mineral composition. The consumption of this type of water is increasing, as it is generally cheaper than natural mineral water to natural mineral waters, spring waters do not have to prove a stable mineral balance. It is not required to state the mineral composition on the label (EFBW/361/EU).

3. Purified water: is originates from any source but has been treated to meet the U.S. Pharmacopeia definition of purified water. Purified water is essentially free of all chemicals (it must not contain more than 10 parts per million of total dissolved solids), and may also be free of microbes if treated by distillation or reverse osmosis. Purified water may alternately be labeled according to how it is treated (USEPA, 2007).

2.3. Water treatment

The quality of drinking water directly affects people's health. The suspension of water, bacteria, viruses, heavy metals, fluoride, chlorides, disinfection byproducts and pesticide residues are all likely to pose a threat to health (Lin *et al.*, 2000). Water should be suitable for human consumption and for all usual domestic purposes, including personal hygiene. Consumption of treated and bottled water is substantially increasing and the number of new companies or small establishments specialized in water treatment is also increasing (WHO, 2011). The combination of conventional drinking water treatment along with disinfection has proven to be one of the major public health advances in modern times. The biological antiseptic quality of Ozone is a powerful disinfectant, effective in treating pathogens, and which oxidizes organic contaminants in much the same way as chlorine.

Deficiency of clean and safe water counts for almost 3.1% of death worldwide (WHO, 2002), which is fore casted to rise over the years. Drinking of contaminated water has become the biggest killer of children less than five years of age (WHO, 2009). According to World Health of Organization (WHO) and the United Nations International Children's Emergency Fund (UNICEF), one child is dying every 15 s due to the direct or indirect consumption of unsafe water (WHO, 2000 and UNICEF, 2013). Further, water crisis causes poverty especially in developing countries, which weakens the Millennium Development Goal (MDG) that depends on the major improvements in access to water (WWDP, 2014).

In order to ensure safe drinking water for all, some membranes such as reverse osmosis (RO), forward osmosis (FO), membrane distillation, and capacitive deionization could be promising in the desalination of both sea and brackish water (Goh,P and Ismail, 2013). But, other conventional water treatment technologies such as physical (boiling, distillation, filtration, sedimentation, microfiltration (MF), Nano filtration (NF), ultrafiltration (UF), sludge storage, and removal, coagulation and flocculation); chemical degradation (ozone, chlorine, chloramine, ultraviolet, H_2O_2 oxidation, solar water disinfection or photo catalytic degradation, supercritical water oxidation, sonochemical degradation); and biological (microbial water sludge treatment) have failed because of their dependence on influent water qualities.(Upad hyayula *et al.*, 2009) observed four difficulties for typical water treatment plants.

Firstly, anthropogenic novel toxic chemicals that harm conventional water treatment plants. Secondly, influent water qualities such as turbidity, temperatures, and pH decrease pathogen's sensitivity and ultimately compromising the treatment plant's efficiency. Thirdly, some bacteria release serious toxic chemicals and affect the overall quality of the treated water. For instance, cyanobacteria release toxins (microcystins and nodularins) while undergoing the treatment process. Finally, the chemical reactions occurring in water treatment plants produce some disinfection byproducts, and the presence of disinfection resistant microorganisms in influent waters compromise water quality standards. Very recently we illustrated some major threats to conventional water treatment technologies (Das *et al.*, 2014). So, these conventional water treatment technologies are experiencing difficulties day-by-day to give 100% pure and safe water and have failed to meet WHO standard of waste water discharge criteria.

There are commonly used four kinds of membrane technologies: microfiltration, ultrafiltration, Nano filtration and reverse osmosis (pore sizes decrease in this order). In water treatment Nano filtration and reverse osmosis are widely used. The main advantages of membrane technologies that they do not require chemicals require low energy and are easy to operate and maintain (Hillie *et al.,* 2006).

Microfiltration(MF): is loosely defined as a membrane separation process using membranes with a pore size of 0.1-10 μm. Materials removed by mf include sand, silt, clays, giardia and cryptosporidium cysts, algae, and some bacterial species. MF is not an absolute barrier to viruses. However, when used in combination with disinfection, mf appears to control these microorganisms in water.

There is a growing emphasis on limiting the concentrations and number of chemicals that are applied during water treatment. By physically removing the pathogens, membrane filtration can significantly reduce chemical addition, such as chlorination. Another application for the technology is for removal of natural synthetic organic matter to reduce fouling potential. In its normal operation, mf removes little or no organic matter; however, when pre-treatment is applied, increased removal of organic material can occur. Mf can be used as a pre-treatment to Ro or NF to reduce fouling potential. Both Ro and NF have been traditionally employed to desalt or remove hardness from groundwater (PA web, 2005 and National Drinking Water Clearing House Web site, 1999).

Ultrafiltration (UF): is a membrane separation technology that separates, purifies, and concentrates solutions between microfiltration and Nano filtration (Zhang, 2000). The pores of ultra-filtration membranes can remove particles of 0.001 – 0.1 µm from fluids. The process can be understood as taking the pressure difference between the two sides of the membrane as the driving force, Under the impetus of static pressure, using ultrafiltration membrane as the filter medium, the solvent in the raw material liquid and the small-molecular-weight solute with smaller pore diameter pass through the ultrafiltration membrane from the high pressure side to the low pressure side, while the large molecular weight solutes are trapped on the high pressure side. That is to say, when water flows through the membrane surface, only water, inorganic salts, and small molecular substances are allowed to permeate the membrane, preventing the passage of macromolecules such as suspended solids, colloids, proteins, and microorganisms in the water for achieving the purpose of purification, separation, and concentration of the solution **(**NIU *et al.*, 2008; Liuqin, 2011; Jianmian *et al.*, 2016).

Physical screening is generally considered to be the main retention mechanism of ultrafiltration membranes. However, sometimes the pore size of ultrafiltration membranes is larger than that of solvents and solute molecules. It should not have trapping effect, but it actually has obvious separation effect. This may be the chemical properties of the membrane surface, such as the cause of electrostatic effects. In summary, there are three main mechanisms of ultrafiltration membrane retention: adsorption once on the surface of the membrane and in the pores, retention in the pores, and removal of mechanical pores on the surface of the membrane (Wenjie, 2006).

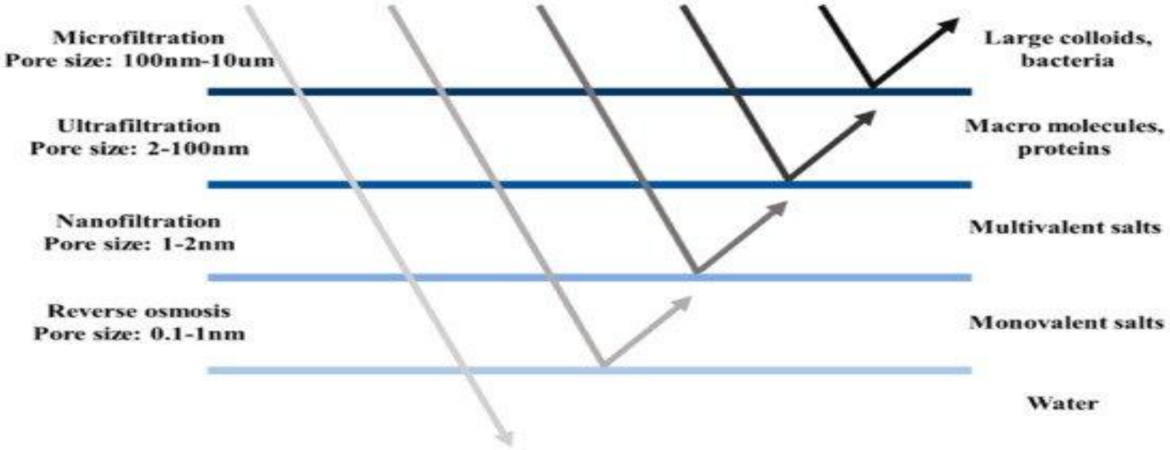

Figure 1: Classification of membranes for water purification in terms of pore size and retained species.

Nano Filter and Reverse Osmosis (NF/RO): retains dissolved contaminants based on size and charge interactions, and hence a generally high NOM retention particularly for humid substances (HS) and biopolymers (Mohsen *et al*., 2003). According to Schäfer *et al.*, (2004) retention of most NOM by NF is due to size exclusion. Therefore, low molecular weight (LMW) organic compounds may permeate and contribute to microbial regrowth. For LMW acids, this retention is charge dependent, while the uncharged molecules like some polysaccharides are rejected by the membrane mainly via size exclusion (Meylan *et al.*, 2007; Schäfer *et al.*, 2004).Therefore, the charge, size, size distribution, and shape of NOM is the most important characteristic for effective removal (Metsämuuronen *et al.,* 2014). It was frequently reported that the hydrophobic fraction of the NOM is mainly responsible for the permeate flux decline and is more strongly rejected by NF membranes than the hydrophilic fraction, which confirms in addition to size exclusion solute-solute and solute-membrane interactions play important role in NOM removal by NF (Metsämuuronen *et al.,* 2014; Nilson and DiGiano, 1996).

Fluoride can in principle be removed by NF/RO (Hu and Dickson, 2006; Tahaikt *et al.*, 2007; Nasr *et al.,* 2013; Shen and Schäfer, 2015) with retention depending on the membrane and water characteristics as well as operating conditions. The main mechanisms involved in fluoride retention are size exclusion and diffusion, with retention decreasing with concentration due to solution diffusion. NF can in fact provide selective removal of fluoride in that smaller ions are more easily retained especially at lower pressures. This was attributed to the strong hydration of the fluoride ion and its high solubility in the water leading to its lower solubility in the membrane (Lhassani *et al.*, 2001; Tahaikt *et al.*, 2008; Shen and Schäfer, 2014; Shen and Schäfer, 2015).

In terms of water quality, some studies investigated the influence of ions, like Ca_2^+ and Cl^- that coexist with fluoride in the ground or surface-waters, on fluoride retention in NF (Nasr *et al.*, 2013) while (Owusu-Agyeman *et al.*, 2017) elucidated the impact of organic matter on fluoride retention. Nano-filtration membranes have a moderate retention for univalent salts and it provides excellent protection from DBP formation (Favre-Reguillon *et al*., 2003; Ermias Kiros, 2018).

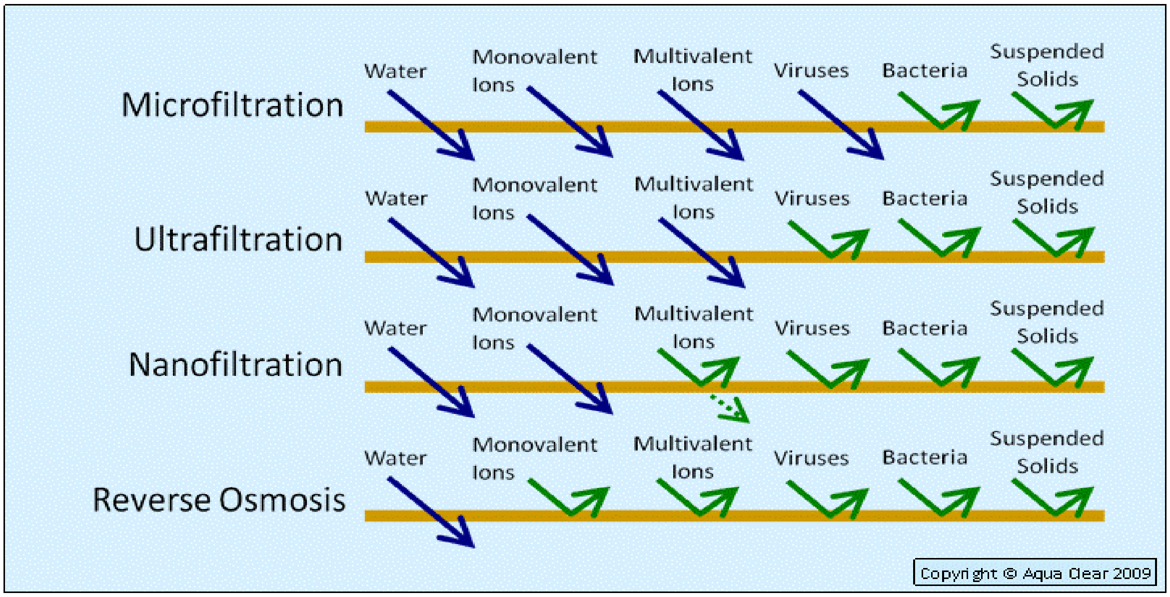

Figure 2: Membrane process characteristic

2.4. Disinfection

Disinfection is of unquestionable importance in the supply of safe drinking-water. It is the last step in the water treatment processes for the protection of public health. Bottled waters should be disinfected and fit for human consumption and compliant to national/international drinking water specifications such as (WHO, 2006). The destruction of microbial pathogens is essential and very commonly involves the use of reactive chemical agents such as chlorine and ozone. Disinfection is an effective barrier to many pathogens (especially bacteria) during drinking-water treatment and should be used for surface waters and for groundwater subject to fecal contamination. (WHO, 2008) 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 (Ermias Kiros G/Mariam, 2018).

Chlorine: Chlorine disinfection has been practiced for over a century and has been credited with saving a significant number of lives worldwide on a daily basis, but it has received a great deal of negative publicity over the past few decades (Nozaic, 2004)**).**One of the first documented uses of chlorine was in 1850 by JohnSnow when he used it to disinfect a water supply in London after an outbreak of cholera (White, 1999). In Taiwan, chlorine is used as the primary disinfectant because of its low cost and its convenience for application in water purification. However, the presence of THMs in chlorinated drinking water can pose a severe health risk due to its potential carcinogenicity (Yang *et al*., 1998). Numerous epidemiological studies have been conducted to investigate the correlations between chlorination by-products and several diseases (McDonald and Komulainen, 2005; WHO, 2005). It has also been reported that the THMs in drinking water will increase the cancer risks of bladder and cause reproductive defects (WHO, 2005; Li *et al*., 2019). Bromate is known to be a byproduct of bromide- containing source waters that undergo ozonation, and has been shown as a contaminant in sodium hypo- chlorite feedstock solutions used for disinfection (Weinberg, *et al* 2003).

Ultraviolet (UV) radiation: Ultraviolet light acts as a powerful sterilizing agent. Ultraviolet (UV) radiation can effectively inactivate various microorganisms in water (Hijnen *et al.*, 2006) and has been increasingly used for water disinfection. UV radiation has numerous advantages over conventional chemical disinfection (e.g., chlorination or ozonation), such as no chemical addition, no harmful disinfection by-products (DBPs) formation, and no introduction of disinfectant-resistance to bacteria (Mori *et al.*, 2007).

Figure 3: UV disinfection apparatus (Ermias Kiros G/Mariam, 2018).

Ozone: Ozone has been applied for water disinfection purposes for almost a century. A recent survey in Switzerland among water works that apply ozone has shown that for 90% of these plants the main reason for its application is disinfection (Courbat, *et al* 1999). Because monitoring for every pathogenic microorganism is not feasible, many countries have adopted the concept of indicator microorganisms (European Community L 330:Directive 98/83/EG, 1998).

The most efficient chemical disinfectant currently applied in drinking water treatment. Even for microorganisms such as protozoa which are difficult to inactivate with other disinfectants. Ozone provides adequate inactivation with reasonable doses and contact times (Von Gunten, 2003). However ozonation treatment of drinking water represents an important potential pathway of bromate formation. In such conditions, drinking water is the primary route of exposure to bromate. In the Netherlands, the exposure of humans to bromate in drinking water, relative to other pathways of exposure, has been reported as approaching 100 percent (Van Dijk-Looijaard and Van Genderen, 2000).

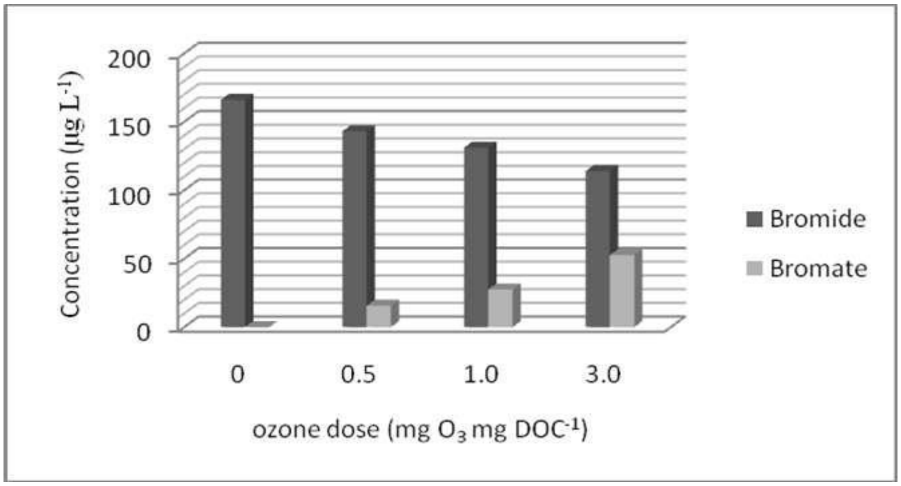

Figure 4. The impact of ozone dose on bromate formation in ground water during ozonation (Petronijevic and Maskovic., 2016).

Surveys on bromate formation in ozonation plants in numerous European countries (Lefebvre *et al.*, 1995; Sacher *et al.*, 1995; Legube, 1996; von Gunten *et al.,* 2000) and the USA have (Daw,2000) been carried out for water works under standard treatment conditions .The disinfection target may vary from one treatment plant to the other. Table1 gives a summary of the five studies performed so far. In European and US American water works, bromate formation was generally below 10 mg/l under these operation conditions.

Table1. Bromate formation in full-scale ozonation plants in Europe and the USA

Country	Number of plants	Bromide range(µg/L)	Bromate range (µg/L)	Number of water works >10 µg/l	Reference
France	10	12-658	<2-19	2	(Lefebvre *et al.*, 1995)
France	32	<20-200	<2-19.6	2	(Sacher *et al.*, 1995)
Germany	4	30-150	<1-12	1	(Legube, 1996)
Switzerland	86	<5-50	<0.5-20	2	(von Gunten *et al.*, 2000)
USA	24	2-180	0.1-40	3	(Daw, 2000)

2.5. Disinfection by-product (DBP) in water

Chemical disinfection processes in drinking water treatment lead to the formation of disinfection byproducts that are undesired due to their potential chronic toxicity (WHO, 1990). Typically, they result from the oxidation of matrix components in the water. There is an ongoing debate on the relevance of disinfection byproducts compared to the risks of waterborne diseases (Ames *et al.*, 1987). Disinfection by-product (DBP) formation is associated with all disinfectants and oxidants, however, the major DBP of concern when using ozone is bromate ($BrO3^-$), a DBP that forms from naturally occurring bromide (Br-) in raw water (Legube *et al.,* 2004).

The formation of unwanted and possibly carcinogenic by-products as a result of the disinfection of drinking water was first recognized by researchers in the 1970s. The first regulations to limit the concentrations of these disinfection by-products (DBPs), a collective term used to describe the suite of compounds resulting from reactions of free chlorine and other oxidants with natural organic matter and other substances in the water, were promulgated by the US Environmental Protection Agency (USEPA) in 1979. Since then, regulations have become more stringent as knowledge of the presence, formation, and health implications of DBPs has increased. More than 500 DBPs have been identified, although only a few have been regulated (McTigue et al., 2014). Disinfection of drinking water has contributed significantly to the reduction of waterborne disease. In spite of disinfection's benefits, DBPs have been shown to have adverse health effects after prolonged (i.e., lifetime) exposures (USEPA, 2006; (AWWA, 2004)). The DBPs most commonly associated with these observed adverse health effects have been halogen substituted organics, typically DBPs containing chlorine or bromine. Although a large variety of complicated halogen substituted DBP compounds are believed to result from the chlorination of drinking water, the only currently regulated DBPs are total tri halo methane's (TTHMs), five of the halo acetic acids (HAA5), bromate, and chlorite (Güler, C. 2007:McTigue et al.,2014).

Disinfection by-product (DBP) formation is associated with all disinfectants and oxidants, however, the major DBP of concern when using ozone is bromate (BrO_3^-), a DBP that forms from naturally occurring bromide (Br^-) in raw water (Legube *et al.*, 2004). Bromate a common ozonation by-product, is a contaminant of concern in drinking water because it induces kidney tumors in laboratory animals (Kurokawa *et al.*, 1990; Butler *et al.*, 2005). The International Agency for Research on Cancer classifies bromate as a possible human carcinogen (IARC 1999).Toxicity testing on experimental animals has consistently shown bromate to induce cancer in rats, mice and hamsters through damage to genetic material (Chipman *et al.*, 1998 and Bull and Cottruvo, 2006).

The U.S. Environmental Protection Agency (USEPA) has set the maximum bromate level in drinking water at 10µg/L(USEPA 1998).European Union law specifies that all member states must enforce a maximum bromate concentration of 10µg/L by 2008 (European Drinking Water Directive). In the UK, the legislation enforcing this standard came into effect in 2003. In the US, regulations also specify a maximum value of 10µg/L. There is some evidence showing that water utilities using hypochlorite solids or liquids for disinfection purposes may add up to 3 µg/L of bromate in to drinking water as a result of the formation of bromate during the manufacture of hypochlorite products (Weinberg *et al.,* 2003).

However, the formation of bromate during disinfection and oxidation is generally only associated with the use of ozone as it has superior oxidizing ability over other commonly used disinfectants. In the presence of ozone, the conversion of bromide to bromate occurs via two complex pathways .The first is through the direct oxidation of bromide from molecular ozone (O_3) to hypobromite (BrO^-), which is then further oxidized to bromate (Haag and Hoigne, 1984). The second pathway occurs from the formation of the hydroxyl radical ($OH^•$) from the decomposition of molecular ozone in water. The hydroxyl radical has an even greater oxidation potential than molecular ozone (Balakrishnan *et al.,* 2002). The hydroxyl radical converts the bromide ion to the bromide radical (Br•) which is then converted to BrO_3^- through further reactions with $OH^•$ or molecular ozone. Bromate formation has been the major barrier in the use of ozone for water treatment where the source water contains bromide, particularly given the challenging targets set for the maximum permissible bromate concentration (Magazinovic *et al.*, 2004).

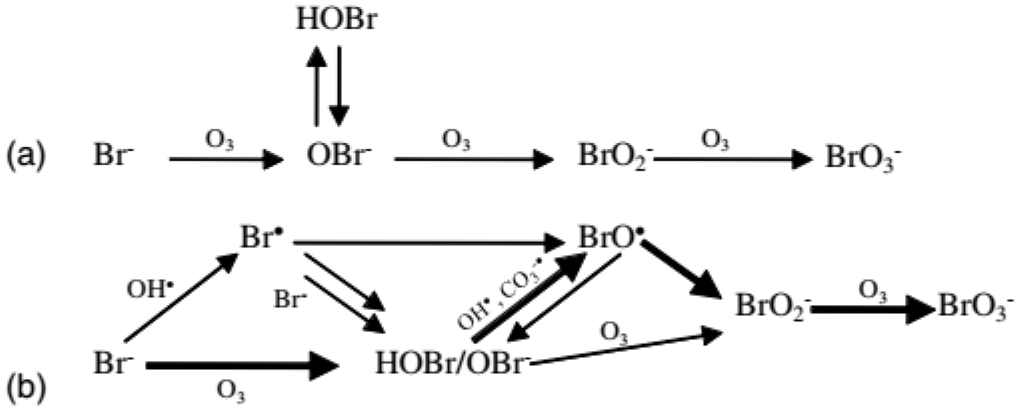

Figure 5: Reactions for bromate formation during ozonation of bromide containing water: (a) reactions with ozone; (b) reactions with ozone and hydroxyl radicals (Von Gunten, 2003).

The formation of bromate during ozonation is strongly dependent on the characteristics of the water to be treated and the amount of ozone contacting the water.

1. **Bromide concentration**: Bromide is oxidized by ozone to bromate; an increase in bromide inevitably leads to an increase in bromate for a constant ozone dose and contact time (Legube *et al.,* 2004). Conversion of bromide to bromate is usually between 10-50 % during ozonation (Song *et al.,* 1996). The propensity to form bromate from bromide is therefore highly dependent on the raw water quality and source and the goals of disinfection.

2. **pH**: As the ozonation pH of the water is increased, the rate of bromate formation increases (Pinkernell and von Gunten, 2001). Bromate formation has been shown to increase from 10 µg/L at pH 6.5 to 50 µg/L at pH 8.2 (Legube *et al.,* 2004) whilst Krasner *et al.* (1993) observed a 60 % decrease in bromate formation for each drop in pH unit. The ozonation pH is widely regarded as being the most effective bromate control strategy at WTW and should be considered the best available treatment for bromate control (Ozekin and Amy, 1997). However, this must be balanced by the increased formation of brominated organic compounds as pH is reduced (USEPA, 1999a). Additionally, the cost of pH reduction may be prohibitive for high alkalinity waters due to the volume of acid required (von Gunten, 2003).

3. **Applied ozone concentration and contact time**: An important consideration in the conversion of bromide to bromate is the specific goal of disinfection (von Gunten *et al.,* 2001). The efficiency of any disinfectant may be characterised by the ‘Ct’ factor (USEPA, 1999b). The relationship between bromate formation and Ct follows a linear function with an increase in Ct leading to an increase in bromate formation (von Gunten and Hoigne, 1996 and Legube *et al.*, 2004).

4. **Dissolved organic carbon (DOC) concentration**: Both the concentration and nature of organic material in water can affect bromate formation (Song *et al.*, 1997); Sohn *et al.*, 2004). During ozonation, any natural organic matter (NOM) present in the water generally reduces bromate formation. This is because ozone and hydroxyl radicals are consumed by the oxidation of organic molecules and therefore taken away from the bromate formation pathways. However, this is not always the case because if a residual ozone concentration is required for disinfection, more ozone may need to be added resulting in similar or in some cases increased concentrations of bromate. The presence of NOM and bromide during ozonation can also lead to the formation of brominated organics. The exact identity of all of these brominated compounds has yet to have been fully established (and are not currently regulated for), but they are believed to be a higher risk to health than chlorine based DBP’s (Song *et al.,* 1997).

5. **Alkalinity**: The presence of inorganic carbon (IC) species increases bromate formation because both carbonate (CO_3^{-2}) and bicarbonate (HCO_3^{-}) species can form the carbonate radical ($CO3^{-\bullet}$) as a result of oxidation by hydroxyl radicals (von Gunten, 2003). Once the carbonate

radical has been formed, this can convert hypobromite into the hypobromite radical ($BrO^{-\bullet}$) and then bromate (Kim *et al.,* 2004).

6. **Ammonia concentration**: The presence of ammonia in water acts as a scavenger of hypo bromous acid (HOBr) during ozonation, an important intermediate in the formation pathway of bromate (Pinkernell and von Gunten, 2001; von Gunten, 2003). HOBr reacts with ammonia to form bromamine compounds, which, in turn, can be converted back to bromide through oxidation by ozone. Ammonia can therefore remove a significant intermediary from the bromate formation path and reduce the amount of bromate formed (Song *et al.*, 1997). Ammonia may be present naturally in waters to be ozonated, or alternatively can be added prior to ozonation as a bromate prevention strategy.

7. **Temperature**: Increased temperature has been shown to increase the rate of bromate formation as a result of increased reaction kinetics (Pontius., 1991; Siddiqui & Amy, 1993; Legube *et al.*, 2004). The effect of temperature has been shown to be more pronounced at higher ozone doses. For example, Galey *et al.* (2004) observed that at an ozone dose of 1 mg/L the bromate formation was 8 μg/L at both 5 and 24 °C whilst at 2.5 mg/L the bromate formation was 22 μg/L at 5 °C and 37 μg/L at 24 °C. Bromate formation is therefore dependent on water temperature and remediation strategies may only need to be considered seasonally where there are big differences in the temperature of the water to be treated. However, it must also be considered that ozone disinfection efficacy is also dependent on temperature.

2.6. Public health goals for chemicals in drinking water

Bromate (BrO_3^-) is a negatively charged polyatomic ion containing one bromine and three oxygen atoms. Typical salts of bromate are potassium bromate ($KBrO_3$) and sodium bromate ($NaBrO_3$). In 1998, the U.S. EPA published an MCL of 0.010 mg/L and an MCLG of zero mg/L for bromate in drinking water, based on a weight of evidence evaluation of both cancer (multiple sites, both sexes, rats) and non-cancer effects. Bromate, as the potassium salt, is listed as a Group 2B possible human carcinogen by the International Agency for Research on Cancer (IARC). Bromate was shown to be mutagenic via in vitro and in vivo studies (Kurokawa *et al*., 1986). In rats, long-term exposure to bromate in drinking water yielded adverse thyroid and kidney effects and inhibited body weight gain (Havelaar *et al.*, 2000). Bromate is not found in drinking water;

however, the bromate ion can form as a disinfection byproduct from the ozonation disinfection process (Cotrubo, 2005), when ozone reacts with relatively non-toxic amounts of bromide in the water to produce the more toxic bromate ion, or when chlorinated water is exposed to sunlight (Macalady *et al.,* 1977 and Kemsley, 2008).

The values for excess cancer risk increased with increasing ozone dose during treatment and showed about one order of magnitude higher than the maximum acceptable level (2×10^{-5}) as per guide lines of US EPA. In the worst case, when the highest ozone dose was used, the excess cancer risk was expected to be about 9.5 per ten thousand people. In Sohn *et al*, (2006) study, the calculated health risk for bromate ranged from 1.4×10^{-4} to 1.3×10^{-3} (average of 4.3×10^{-4}) for the ten source waters.

Table 2: Health risks (excess cancer risk and chemical toxicity risk) (procentile 95th) due to ingestion of bromate in ozonated water (Petronijevic, M., & Maskovic, P, 2016)

Ozone Dose (MgO_3 mg DOC/l)	Excess cancer risk ($X\ 10^{-4}$)	Chemical Toxicity risk (LADD)	Hazared quioent (HQ)
0.5	2.96	0.4	1.0
1.0	5.22	0.715	1.9
3.0	9.5	1.368	3.6

To evaluate the chemical toxicity risk of bromate, the lifetime average daily dose (LADD) of bromate through ingestion was estimated at different ozone doses and compared it with the reference dose (RfD) of 0.372 µg/ kg day^{-1} and there by produced a hazard quotient (Table 2). The life time average daily dose (LADD) increased (0.400 - 1.368 µg/ kg^{-1} day^{-1}) during ozonation, by considering the body weight as 70 kg of an adult Serbian reference man. The mean of hazard quotient (LADD/RfD) was also found to be slightly greater than unity indicating that bromate in drinking water is under alarming situation from the chemical toxicity point of view. In the worst case, the exposure dose determined to be 3.6 µg/ kg day^{-1}which is 3 - 4 times higher than RfD. Approximately, the same number of times bromate content is higher than the reference value of 10 µg/ L. All conclusions are in accordance with the regulations; the risk is significantly increased because the bromate content is up to five times higher than the exposure limits, which are also based on health risks (Petronijevic, M., & Maskovic, P, 2016).

However, ozonation tends to oxidize bromide to bromate, which presents a potential problem, since bromide is naturally present in spring waters. Bromate is a potential carcinogen, even at low microgram per liter (µg/L) level: a Maximum Admissible Concentration (MAC) of 10 µg/L bromate in drinking waters is recommended by the European Commission (in Directive 98/83), by the US EPA, the WHO. And Nestle Waters International (NWI).

2.7. Fluoride

The element fluorine is the lightest member of the halogen group and is the most electronegative. As such, it is the most reactive of all elements (Brindha and Elango, 2011). Fluorine does not occur in the environment naturally in its elemental state but rather as the negatively charged fluoride ion, F^- because of its high tendency to react and combine with other elements forming strong electronegative bonds and producing ionic compounds (Ayoob and Gupta, 2006). Fluoride occurs naturally in same ground water and is often introduced into drinking water for the prevention of tooth decay. Excessive amount of fluoride are however objectionable and can cause tooth discoloration.

In small amounts, fluoride is beneficial for oral health because it reduces the ability of plaque bacteria to produce acid that damages teeth. Fluoride also improves the chemical structure of the enamel by making it more resistant to acid attack that causes tooth decay (Ayoob and Gupta, 2006). For these reasons, fluoride is added to toothpaste; in some countries, to drinking water (Edmunds and Smedley, 2005; Sun *et al*., 2013). However, prolonged exposure to high doses of fluoride is detrimental because of the risk of fluorosis. In drinking water has a profound effect on teeth and bones (Mohapatra *et al*, 2009). The most common symptom of dental fluorosis is mottling, and ultimately, destruction of teeth. With exposure to high concentrations for prolonged periods, fluoride may accumulate in bones, leading to crippling skeletal fluorosis. Once developed, the symptoms of fluorosis are irreversible (Ayoob and Gupta, 2006).

The probability of occurrence of high fluoride concentration in ground and surface water was detected in various countries such as India, China, Argentina, Mexico, and in several African countries (Amini *et al*.,2008). In Ethiopia, especially in the Ethiopian Rift Valley, water contaminated with fluoride has led to a serious public health problems (Kloos and Tekle-Haimanot, 1999, Tekle-Haimanot, 2005 and Tekle-Haimanot *et al.*, 2006).

Fluoride is mostly absorbed into the human body by drinking or cooking with water containing fluoride (Tekle-Haimanot *et al.*, 2006). Excess fluoride intake can cause dental and skeletal fluorosis. Symptoms range from irregular brown patches on teeth to deformation of bones, limitation of joint movements, and even crippling (crippling fluorosis) in the last stage of the disease, accompanied by serious psychosocial impacts (Tekle-Haimanot, 2005). According to the limits issued by the World Health Organization (WHO) that fluoride ions have a beneficial effect when they are about 0.7 mg/L, but very dangerous if more than 1.5 mg/L.

Table 3.Effect of prolonged use of drinking water on human health, related to fluoride content (Mohapatra *et al.*, 2009)

F^- concentration, (mg/L)	**Health outcome**
<0.5	Dental caries
0.5–1.5	Optimum dental health
1.5–4.0	Dental fluorosis
4.0–10	Dental and skeletal fluorosis
>10.0	Crippling fluorosis

3. MATERIALS AND METHODS

3.1. Chemicals

For physicochemical analysis, mainly used chemicals include analytical reagent potassium bromate (Sigma-Aldrich, 309087 and VWR, 1.04912.0100), concentrated hydrochloric acid (37%)(VWR, 1.00317.1000), methylene blue (VWR, 1.59270.0100), concentrated sulfuric acid (98%), ammonium chloride (NH_4Cl), ammonium hydroxide (NH_4OH), ammonia solution 25%, Ethylene Diamine Tetra Acetic Acid (EDTA)**,** eriochrome black T (EBT), methyl orange, lithium hydroxide (Fluoride No1) tablet, and boric acid (Fluoride No 2) tablet.

Plate Count Agar (PCA) was used for aerobic plate count whereas Lauryl Tryptose Broth (LTB) and Brilliant green bile (BGB) broth were used for total coliform count. Ethanol (70%) was used for disinfection.

3.2. Instruments

Instruments used in this study included: UV-Visible Spectrophotometer (Spectroquant® Prove 300 UK), pH meter (Model: ST300, Ohous CORPORATION, USA), Total Dissolved Solids (TDS) and electrical conductivity (EC) meter (Model: ST300C, Ohous CORPORATION, USA), and fluoride photometer 71000 UK, turbidity turbido-meter UK. Whereas, Incubator, dry oven, autoclave, hot plate, colony counter, analytical balance, and bio-safety cabinet were used for microbiological analysis.

3.3. Study design

Completely Randomized Design (CRD) was used for the experiment. The statistical analysis of the bromate, fluoride level, microbiological and Physico-chemical parameters was using one sample t-test. Analyses were conducted using SPSS version 20.0. Stastistix8 also used for correlation of bromate with other Physico- chemical parameters.

3.4. Study area

The present study was carried out at Addis Ababa, which is a capital city of Ethiopia. The population of the city is currently estimated to be 4.6 million. It is located in the geographical coordinate 30-150 N and 330-480 E with an estimated area of 1,104,300 sq km (FDREMH, 2011).

Almost all packed brand water companies are established in and nearby Oromiya special zones, Debre Berhan area, and Gurage areas, so there is access of getting almost all water types consumed in Addis Ababa. The sampling was conducted at different locations of the Addis Ababa city from supermarkets distributer cars and shops which were selected randomly. Currently, there are more than 70 packed brand water companies certified by the Ethiopian Conformity Assessment enterprise.

3.5. Water samples collection

Thirty local brand packed water samples were brought for the present study. Each of the drinking packed brand water was randomly purchased from supermarket, kiosks, distributing cars, cafes and restaurants from different locations in Addis Ababa manufactured, in different regions during January and February 2020.

Table 4. Sample code, water type and treatment type of the collected packed water brands of different brand waters

Sample code	Type of water	Treatment
Bpw1	Mineral	Ozone
Bpw2	Mineral	Ozone
Bpw3	Mineral	Ozone & UV before and after
Bpw4	Mineral	Ozone
Bpw5	Mineral	Nano filter & Ozone
Bpw6	Natural purified	Ozone
Bpw7	Natural purified	Ozone
Bpw8	Natural purified	Ozone
Bpw9	Natural purified	Ozone
Bpw10	Natural purified	Ozone & UV after ozone
Bpw11	Natural purified	Ozone & Nano
Bpw12	Natural purified	Ozone & UV after ozone
Bpw13	Natural purified	Ozone
Bpw14	Natural purified	Ozone & UV after ozone
Bpw15	Natural purified	Ozone
Bpw16	Natural purified	Ozone & UV after ozone
Bpw17	Natural purified	Ozone
Bpw18	Natural purified	Ozone
Bpw19	Natural purified	Ozone
Bpw20	Natural purified	Ozone & UV after ozone
Bpw21	Natural purified	Ozone & UV after ozone
Bpw22	Natural purified	Ozone
Bpw23	Natural spring	Ozone
Bpw24	Natural spring	Ozone & UV before ozone
Bpw25	Natural spring	Ozone
Bpw26	Natural spring	Ozone
Bpw27	Natural spring	Ozone
Bpw28	Natural spring	Ozone & UV
Bpw29	Natural spring	Ozone, UV & Nano
Bpw30	Natural spring	Ozone & UV after ozone

Bpw: Brand packed water; UV: Ultraviolet

Once all the samples were brought to laboratory, at room temperature with their original sale containers until analysis was carried out. Information such as sample code, type of water and treatment type are presented in Table 4. The holding capacities of sampled containers were 0.5litter and 1 litter. Triplicate samples were collected by three times round.

3.6. Physicochemical analysis

Bromate

Bromate was measured using UV/VIS Spectrophotometer Model: Spectroquant® Prove 300 UK. The instrument was calibrated from 1 mg/L and 10 mg /L bromate solution prepared (5 – 10 – 20 – 30 – 40) µg/L bromate calibration solution respectively and verified using10 µg/L and 20 µg/L bromate solution from different stock for checking calibration. 20 mL water sample was introduced to a 25 mL plastic disposable tube under a fume hood and added 1 mL of methylene blue solution from 0.02 g/L and 1.5 mL of hydrochloric acid 37 %. Closed the test tube and mixed carefully .set for 10 minute in order to homogenize. After that the solution was transferred into 50 mm cell and introduced to the instrument. The measurement was performed in triplicate by using spectrophotometric method.

Fluoride

Fluoride content of the water was determined by using photo meter instrument was made using Model: photometer 7100. The instrument was calibrated with distilled water. From 10 mL water sample was added one Lithium hydroxide (fluoride No 1) codeNE110NS and boric acid (fluoride No 2) code NE110NS. Fluoride No 2 tablet was crushed and mixed to dissolve respectively and it was stood 5 minute to allow full colour. Then the sample was transferred to a 10 mL palintest and inserted to the photometer to measure the result and the measurement was performed in triplicate by using ES ISO10359-1 test method.

Total dissolved solids (TDS) and electrical conductivity (EC)

TDS and EC measurements were conducted using conductivity meter Model: ST300C, Ohous CORPORATION, USA. The instrument was calibrated with distilled water. 30 mL water sample was transferred to a 50 mL plastic beaker and put on the plate and the instrument sensor was inserted to the beaker to measure the parameters. And the measurement was performed in triplicate by using ES609 test method.

pH

The pH values of the packed water samples were measured using a pH meter Model ST300, Ohous CORPORATION, USA in triplicate. The pH electrode was rinsed with deionized water and calibrated with pH 4.00, 7.00 and 10.00, standard buffer solutions. The pH electrode was rinsed with deionized water to avoid contamination of the buffers. The pH values of the packed water samples were measured by inserting the electrode in 50 mL of the packed water sample in a beaker using the pH meter in triplicate by using ESISO10523 test method.

Total alkalinity

Alkalinity was determined by titrating with standard sulfuric acid (0.02 M) using phenolphthalein and bromocresol indicators. 25 mL of bottled sample was transferred into conical flask and phenolphthalein and bromocresol indicators were added to the flask. Finally, the solution was titrated with H_2SO_4. The concentration of total alkalinity was calculated by using equation 1.

$$\text{Total alkalinity as CaCO3} = \frac{\text{volume of sulfuric acid x molarity of sulfuric acid x 50x1000}}{\text{volume of the sample}} \tag{1}$$

Total hardness

The total hardness of the water was determined by complexometric titration using EBT indicator and ammonium, ammonium chloride buffer solution. The solution was stirred until all the solids were dissolved, and its pH was found to be 10. Before the titration, the burette was rinsed with EDTA solution and filled with 0.02 M EDTA standard solutions. An aliquot of 25 mL sample water was transferred to a conical flask and then 2 drops of EBT indicator and 1 mL buffer solution were added into the beaker. Finally the solution was titrated against EDTA solution which was filled in the burette. The same procedure was used for three blank samples. The total hardness of the water sample was calculated by using equation 2 as calcium carbonate (mg/L**)**.

$$\text{Total hardness as CaCO3} = \frac{\text{volume EDTAx molarity EDTAx50x1000}}{\text{Volume of sample}} \tag{2}$$

Turbidity

The turbidity of the water was determined by compact Turbido meter instrument (Model: CT12, UK palintest). The instrument was calibrated with distilled water. Water sample was transferred to a 10 mL palintest and inserted to the turbido meter to measure the values and the measurement was performed in triplicate.

3.7. Microbiological analysis

Aerobic plate count: 23.5g of plate count agar was mixed with one liter of distilled water and heat the media till up to homogenize and then sterile for 121^{o}C for 15 minutes. Petri dish was washed with detergent and soaks it for 1.30 hours and then rinsed with water. Then dry in the oven at 175^{O}C for one hour. After that the dishes was taken out and keep it in safety cabinet. 1ml of sample was transferred in to the sterilized petri dish and added 15-20 ml of media. Incubate at 35^{0}c+/-2^{0}c for 48 hours performed in triplicate.

Total coliforms: 35.6g of LSTB was dissolved in one liter of distilled water and heat it to <50^{0}c to homogenize well and sterile for 121^{O}C for 15 minutes. The test tubes and drum tube was washed with detergent and soak it for 1.30 hours and rinsed with water. Dry at 175^{O}C for one hour. The test tubes and drum tube was taken out and keep it in safety cabinet.1ml of sample was added 10 ml of LSTB in to each three test tubes and incubate at 30^{0}c+/-2^{0}c for 72 hours performed in triplicate . Using most probable number to count the total coliform.

4. RESULTS AND DISCUSSIONS

In this study the level of bromate, fluoride and microbial load on Ethiopian packed water brands treated using ozone, ozone + UV, and ozone +Nano filter were evaluated. The microbial load are compared with two standards (CES 99, 2019 and WHO, 2008) and three treatment types (Table 5). The level of Physico-chemical parameters are compared with local and international standards; CES 99, 2019, EPA, 2018 and WHO 2017 (Table 6) whereas the levels of bromate and fluoride are compared with the label of packing (Table 7). The results of level of bromate analysis are compared with other four countries listed by Urs von Gunten (2003), (Table 8).The final two tables Table 9 and Table 10 show correlation of Physico-chemical parameters in the bromate formation and bromate value in water type and treatment.

Microbial load of packed water brands in Ethiopia processed with different treatments

The microbiological analysis of the different brand water samples are shown in table 5. All aerobic bacterial count and coliform result were on the standard in different brands of packed water samples. WHO (2008), CES99 (2019) and CES151 (2015) for aerobic plate count in water is <100cfu/mL. The present study shows that the aerobic plate count was claimed with in the standard. Total Coliforms are not likely to cause illness, but their presence indicates that water may have been contaminated by more harmful microorganisms. The CES99 (2019) and CES151 (2015) and WHO (2004a) sets zero detection per 100 ml for total coli form bacteria. As table 5 shows the coliform was undetectable in all samples. In this study all packed water sample result has with in the standard in ozone, ozone +UV and ozone + Nano filter technology treated packed water. So the above result indicates safe and potable as the microbiological point of view.

Table 5. Microbial load of different packed water brands in Ethiopia treated with ozone, UV, and nano filter

	Specification			Parameters	
				APC cfu/mL, max	Coliform/mL
	CES99, 2019			<100	Undetectable
	CES151, 2015			<100	Undetectable
Brand Code	WHO ,2008			<100	Undetectable
	Treatment				
	Ozone used	Ozone +UV used	Ozone +Nano filter used		
Bpw1	Yes	No	No	<100	Undetected
Bpw2	Yes	No	No	<100	Undetected
Bpw3	Yes	Yes	No	<100	Undetected
Bpw4	Yes	No	No	<100	Undetected
Bpw5	Yes	No	Yes	<100	Undetected
Bpw6	Yes	No	No	<100	Undetected
Bpw7	Yes	No	No	<100	Undetected
Bpw8	Yes	No	No	<100	Undetected
Bpw9	Yes	No	No	<100	Undetected
Bpw10	Yes	Yes	No	<100	Undetected
Bpw11	Yes	No	Yes	<100	Undetected
Bpw12	Yes	No	No	<100	Undetected
Bpw13	Yes	No	No	<100	Undetected
Bpw14	Yes	Yes	No	<100	Undetected
Bpw15	Yes	No	No	<100	Undetected
Bpw16	Yes	Yes	No	<100	Undetected
Bpw17	Yes	No	No	<100	Undetected
Bpw18	Yes	No	No	<100	Undetected
Bpw19	Yes	No	No	<100	Undetected
Bpw20	Yes	Yes	No	<100	Undetected
Bpw21	Yes	Yes	No	<100	Undetected
Bpw22	Yes	No	No	<100	Undetected
Bpw23	Yes	No	No	<100	Undetected
Bpw24	Yes	No	No	<100	Undetected
Bpw25	Yes	No	No	<100	Undetected
Bpw26	Yes	No	No	<100	Undetected
Bpw27	Yes	No	No	<100	Undetected
Bpw28	Yes	Yes	No	<100	Undetected
Bpw29	Yes	Yes	Yes	<100	Undetected
Bpw30	Yes	No	No	<100	Undetected

PCA plate count agar, CES Compulsory Ethiopian standard

Table 6. Physico-chemical qualities of packed water brands in Ethiopia

	Parameter							
specification	Bromate (µg/L)	Fluoride (5mg/L)	E.C (µs/cm)	TDS (mg/L)	PH	Turbidity (NTU)	TH (mg/L)	TA (mg/L)
WHO 2017	10	1.5	300	500	6.5-8.5	5	500	200
EPA 2018	10	2.0	-	500	6.5-8.5	5	-	-
CES 99 2019	-	1.5	1500	1000	6.5-8.5	5	300	600
CES151	-	1	-	150-1500	6.0-8.5	5	400	75-600
Brand Code								
Bpw1	3.8.00±0.78	0.43±0.05	138.30 ±2.00	92.00 ± 0.00	7.30±0.15	0.01±0.00	65.60±0.58	49.00±1.00
Bpw2	28.60±1.60	0.78±0.05	197.80±0.20	130.10±0.23	7.70±0.15	1.97±0.16	64.00 ±0.00	80.00±0.00
Bpw3	7.90±1.40	0.30 ±0.05	183.00±0.00	120.30±1.10	7.80±0.05	0.01±0.00	93.30±2.30	65.70±0.58
Bpw4	25.20±0.10	0.4.00±0.10	202.80±2.70	136.20±0.40	8.1±0.20	0.01±0.00	24.00±0.00	66.00± 0.00
Bpw5	26.00±0.80	0.09±0.01	188.90±1.65	115.00±1.70	7.8±0.15	0.01±0.00	64.00±0.00	100.00±0.00
Bpw6	20.60±1.20	0.60±0.00	279.00±0.80	185.10±1.20	8.0±0.10	0.17±0.01	20.00±0.00	80.00 ±0.00
Bpw7	4.70±0.50	0.10±0.00	58.20±0.17	38.30±0.30	6.8±0.10	0.01±0.00	16.00±0.00	20.00±0.00
Bpw8	32.60±0.70	0.60±0.10	282.30±1.10	185.60±0.75	7.6±0.65	0.01±0.00	64.7.00±1.10	19.3.00±1.10
Bpw9	9.10±0.95	0.23±0.05	69.20±3.30	44.00±4.00	6.8±0.10	0.07±0.01	24.30 ±0.50	20.00±0.00
Bpw10	4.50±1.00	0.04±0.01	13.60±2.00	8.70±1.20	7.6±0.65	0.01±0.00	BDL	10.00±0.00
Bpw11	3.10±0.60	0.30±0.15	49.00±1.00	32.40±0.70	7.50±0.00	0.01±0.00	20.00±0.00	18.00±2.00
Bpw12	BDL	0.17±0.05	53.10±2.70	35.00±1.8	6.4.0±0.10	0.02±0.01	17.30 ±2.30	18.00±0.00
Bpw13	BDL	0.10±0.03	33.30±0.23	22.00±0.00	7.20±0.05	0.01±0.00	8.00± 0.00	16.00±0.00

Bpw14	BDL	0.23±0.06	35.60±0.45	23.50±0.30	7.20 ±0.00	0.03±0.02	9.70±1.50	11.00±1.00
Bpw15	11.70±3.00	0.30±0.20	277.00±3.00	182.60±2.00	7.20±0.005	0.01±0.00	95.30±1.10	73.30±1.50
Bpw16	BDL	0.30±0.20	250.50±1.50	158.30±3.00	8.10±0.05	0.01±0.00	96.00±2.00	20.00±0.00
Bpw17	3.70±1.70	0.10±0.00	4.50±0.60	3.00±0.40	6.40±0.45	0.01±0.00	6.00±2.00	8.00±2.00
Bpw18	5.20±1.50	0.20±0.00	14.80±1.70	9.30±1.30	6.10±0.015	0.01±0.00	4.00±0.00	10.00 ±0.00
Bpw19	3.70±1.70	0.20±0.14	9.30±0.60	6.10±0.40	5.90±0.40	0.08±0.01	BDL	8.00 ±0.00
Bpw20	9.20±1.30	0.23±0.05	56.50±2.90	35.20±3.80	7.50±0.15	0.10±0.007	18.70±2.30	40.00±0.00
Bpw21	0.80±0.30	0.10±0.00	23.50±1.30	15.50±0.80	6.80±0.05	0.01±0.00	BDL	20.00±0.00
Bpw22	2.40±0.00	0.07±0.03	5.10±0.25	3.60±0.35	6.30±0.00	0.06±0.04	4.70±1.10	8.00 ±2.00
Bpw23	6.20±1.10	0.30±0.15	47.20±0.70	27.70±2.20	7.40±0.00	0.01±0.00	8.00±0.00	18.00±0.00
Bpw24	11.10±0.50	0.10±0.03	186.60±0.50	25.80±3.10	6.80±0.05	0.10±0.00	12.00±2.00	8.00±0.00
Bpw25	6.50±2.00	0.13±0.05	113.71±0.75	74.60±1.10	7.70±0.95	0.05±0.02	18.70 ±1.10	32.30±0.50
Bpw26	6.00±1.30	0.60±0.40	68.70±4.00	47.00±2.60	7.50±0.00	0.01±0.00	21.30±2.30	80.00±0.00
Bpw27	5.50±0.70	0.20±0.10	117.90±0.15	76.80±1.20	7.60±0.40	0.01±0.00	50.00±0.00	37.70±0.58
Bpw28	15.40±0.50	0.23±0.05	200.30±1.50	33.70±2.10	6.50±0.15	0.02±0.01	18.70 ±1.20	15.30±1.20
Bpw29	4.70±1.70	0.10±0.02	26.60±1.50	17.30±1.00	6.60±0.30	0.11±0.00	BDL	9.70 ±1.50
Bpw30	5.50±1.50	0.20±0.00	116.90±0.36	77.10±1.10	7.50±0.05	0.07±0.01	18.00±0.00	16.00±0.00

BDL: Below detection limit.

All data are expressed of mean ± SD (n=3), the result are compared with the standard value for further discussion.

Bromate

Despite the fact that the European Commission in Directive 98/83, Health Canada (1999), WHO (2005), U.S. EPA (2006), DPH (2008), WHO (2008), WHO (2011) and NWI recommend the bromate maximum admissible concentration (MAC) value is 10µg/L as acceptable for drinking water, the concentration of bromate in the study ranged from 0.8µg/L to 32.6µg/L.

In the study, the concentration of Bromate in eight samples (26.66%); Bpw2, Bpw4, Bpw5, Bpw6, Bpw8, Bpw15, Bpw 23 and Bpw27 were higher than the maximum recommended limit. High concentration of Bromate is not safe for drinking purpose because it can cause cancer according to USEPA (1998) and WHO (2005). Bromate has been identified as a possible human carcinogenic agent. The level of bromate in drinking water is strictly controlled at 10µg/L in most developed countries according to Jarvis *et al.,* (2007). The remaining of 22 (73.3%) brands of packed water value was within the standard.

Fluoride

The recommended acceptable limit of fluoride concentration for drinking water is below 1.5mg/L according to WHO (2017) and CES99 (2019). Exceeded level of fluoride will adversely affect dental health (enamel fluorosis). Similarly, with too low concentration of fluoride, optimal caries prevention will not be achieved according to Cochrane *et al.,* (2006). Fluoride in drinking water has a profound effect on teeth and bones. A small level (<0.5 mg/L) dental caries, (1-1.5 mg/L) this strengthens the enamel. The range of 1.5- 4 mg/L result in dental fluorosis whereas, with prolonged exposure at still higher fluoride concentrations (4-10 mg/L) dental fluorosis progresses to skeletal fluorosis according to Mohapatra *et al*, (2009).The investigated result of the entire packed brand waters lie below the maximum acceptable limit. Which is the ranged from 0.04 mg/L to 0.78 mg/L. But, according to Mohapatra *et al*, (2009) in the present study shows 86.6% the fluoride value was <0.5 mg/L which can cause of dental caries. The remaining13.3% was within the range.

Electrical Conductivity (EC)

The values of electrical conductivity recorded in the present study were the range between 4.5µs/cm to 282µs/cm. The lowest recorded in Bpw30 and the highest recorded BPw19. According to WHO (2017) and CES99 (2019) the maximum permissible limit is 300µs/cm and

1500µs/cm respectively. The investigated parameters of all the packed brand waters lie below the maximum acceptable limit set by WHO (2017) and CES99 (2019).

Total dissolved solid (TDS)

The concentration of total dissolved solid in the study ranged 3 mg/L - 185.6 mg/L. According to WHO (2017) and EPA (2018), the recommended maximum permissible limit of TDS for drinking water is below 500 mg/L. Whereas, CES99 and CES151 recommends 1000 mg/L and 150 mg/L-1500 mg/L, respectively. However according to Mahajan, *et al* (2006), Lower values of total dissolved solids (TDS), hardness and electrical conductivity than the recommended limits of WHO showed that water was deficient in essential minerals. Minerals like magnesium, potassium, calcium and fluoride were present in some cases in such a low concentration that water seemed to be as distilled water. In the present study can be claimed that these brands of packed water are suitable for drinking depending on WHO (2017), EPA, (2018) and CES99, (2019). But, according to CES151, (2015) standard all five brand of mineral water below the permissible limit.

pH

The pH of the 30 brands of packed water ranged 5.9-8.1 where the lowest recorded for Bpw22 and the highest value was recorded for Bpw4 and Bpw16 packed natural purified water, (Table 8). The permissible range of pH in a drinking water should be in the range 6.5-8.5 according to Mahajan *et al.,* (2006), WHO (2017) and CES99 (2019). Whereas CES151 (2015) 6.0-8.5. In the present study, pH value of five (16.6%) Bpw12, Bpw17, Bpw18, Bpw19 and Bpw22 natural purified brand water is lower than from the minimum range of drinking water set by Mahajan *et al.,* (2006), (WHO (2017) and CES99 (2019). The remaining 25 (83.3%) of brand water have lies within the range according to the recommended standards. whereas according to CES151 (2015) all five mineral water claimed with the permissible limit.

Turbidity

The concentration of turbidity reported by CES151 (2015), WHO (2017), EPA (2018), CES99 (2019) and Ismail *et al.,* (2013) don’t more than 5 NTU in drinking water. Turbidity, which is caused by suspended chemical and biological particles, can have both water safety and aesthetic implications for drinking water supplies according to WHO (2017). In this study the value of turbidity in all brand packed drinking water was found below the 5 NTU. The reading of the tested samples was the range from 0.01NTU to 1. 97NTU.The maximum turbid value of in this study was 1.97NTU in Bpw2 which is higher than within compared to the other 29 brand packed water sample.

Total Hardness

According to WHO (2011) the maximum permissible limit values of total hardness for drinking water is <500 mg/L, whereas CES151 (2015) and CES99 (2019) 400 mg/L and 300 mg/L respectively. Water containing calcium carbonate at the concentrations below 60 mg/L is generally considered as soft, 60 mg/L -120 mg/L moderately hard, 120 mg/L -180 mg/L hard and more than 180 mg/L very hard according to WHO, (2009). In the entire brand water sample according to WHO, (2009) 76.6% was as soft and 23.3% as moderately hard water. The total hardness value in the present brand water samples were ranged from 4 mg/L to 96 mg/L and four samples not detected as calcium carbonate.

Total Alkalinity

The maximum concentration limit of total alkalinity for drinking water is 200 mg/L according to CES (2013) and WHO (2017) whereas CES 151 (2015) and CES99 (2019) is 75 mg/L - 600 mg/L and 600 mg/L respectively. In the present study the concentration of total alkalinity ranged from 8 mg/L to 100 mg/L. According to CES 151, (2015) from five mineral water three samples was below 75 mg/L.

Table 7.Comparistion of bromate and fluoride level of the different branded packed water

Brand code	BrO_3-(µg/L)		Fluoride (mg/L)	
	On the label	Analysis result	On the label	Analysis result
Bpw1	No	3.80 ±0.78^{b-d}	No	0.43 ±0.05^{de}
Bpw2	No	28.60±1.60^{m}	No	0.78±0.05^{f}
Bpw3	No	7.90±10.40^{fg}	0.3	0.30 ±0.05^{a-d}
Bpw4	No	25.20±0.10^{l}	No	0.40 ±0.10^{c-e}
Bpw5	No	26.00±0.80^{l}	No	0.09±0.01^{ab}
Bpw6	No	20.60±1.20^{k}	No	0.60±0.00^{ef}
Bpw7	No	4.70 ±0.50^{b-e}	No	0.10±0.00^{ab}
Bpw8	No	32.60±0.70^{n}	0.91	0.60±0.10^{ef}
Bpw9	No	9.10±0.95^{gh}	No	0.23 ±0.05^{a-d}
Bpw10	No	4.50 ±0.10^{b-e}	0.04	0.04±0.01^{a}
Bpw11	No	3.10±0.60^{bc}	No	0.30 ±0.15^{a-d}
Bpw12	No	BDL	0.5	0.17±0.05^{ab}
Bpw13	No	BDL	0.13	0.10±0.03^{ab}
Bpw14	No	BDL	No	0.23 ±0.06^{a-d}
Bpw15	No	11.7±3.00^{i}	No	0.30 ±0.20^{b-d}
Bpw16	No	BDL	No	0.30 ±0.20^{b-d}
Bpw17	No	3.70 ±1.70^{b-d}	No	0.10±0.00^{ab}
Bpw18	No	5.20 ±1.50^{c-e}	No	0.20 ±0.00^{a-c}
Bpw19	No	3.70 ±1.70^{b-d}	No	0.20 ±0.14^{a-c}
Bpw20	No	9.20±1.30^{gh}	0.16	0.23 ±0.05^{a-d}
Bpw21	No	0.80±0.30^{a}	No	0.1±0.00^{ab}
Bpw22	No	2.40±0.00^{ab}	No	0.07±0.03^{ab}
Bpw23	No	6.2±1.10^{ef}	No	0.30 ±0.15^{a-d}
Bpw24	No	11.1±0.50^{hi}	0.02	0.10±0.03^{ab}
Bpw25	No	6.5±2.00^{ef}	No	0.13±0.05^{ab}
Bpw26	No	6.00 ±1.30^{d-f}	No	0.60±0.40^{ef}
Bpw27	No	5.50 ±0.70^{c-e}	No	0.20 ±0.10^{a-c}
Bpw28	No	15.40±0.50^{j}	No	0.23 ±0.05^{a-d}
Bpw29	No	4.70 ±1.70^{b-e}	0.02	0.10±0.02^{ab}
Bpw30	No	5.50 ±1.50^{c-e}	0	0.20 ±0.00^{a-c}

BDL: Below detection limit

All the given values are means of three determinations ± standard deviation (SD), mean values in the same column with different superscripts are significantly different at ($P<0.05$) using Duncan's multiple range test .All data are expressed mean ± SD (n=3).

Table 7 shows the level of Bromate and fluoride concentrations on the label of the packing and analyzed result. As the table shows the level of bromate concentrations on the label (packing) was not reported in all brand water sampled that sold in the market.

The concentration fluoride for drinking water is known by WHO (2017) and CES99 (2019). In the present study 70% of brand packed water sample sold in the market was not reported on the label of the packing. Whereas 10 brands (30%) Bpw3, Bpw8, Bpw10, Bpw12, Bpw13, Bpw16, Bpw19, Bpw24, Bpw23 and Bpw29 of the sample were reported on the label.

Table 8.Comparison of the bromate results obtained from the present study with other countries of Bromate formation in full-scale ozonation plants in Europe and the USA.

Country	Number of plants	Bromate range µg/L	Number of water works >10 µg/L	Reference
France	10	<2-19	2	(Lefebvre et al., 1995)
France	32	<2-19.6	2	(Sacher et al., 1995)
Germany	4	<1-12	1	(Legube, 1996)
Switzerland	86	<0.5-20	2	(Von Gunten *et al.*, 2000)
USA	24	0.1-40	3	(Daw,2000)
Ethiopia	30	0.8-32.6	8	Present study

We can see from table 8, that there are a lot of variations number of water works >10 µg/L of the Ethiopian packed brand water samples compared with other countries sample. The disinfection target may vary from one treatment plant to the other Von Gunten, (2003). Table 8 gives a summary of the six studies performed so far. In European and US American water works, bromate formation was generally below 10µg/l. However in France according to Lefebvre *et al.*, (1995) and Sacher *et al.*, (1995), the bromate value from 10 pant 20% and from 32 plant 6.6% respectively. In Germany 25% from 4 plant Legube, (1996).In Switzerland 2.3% from 86 plant von Gunten *et al.*, (2000). In USA 12.5% from 24 plant Daw, (2000). When compared to with other countries in Ethiopia 26.6% from 30 pants which is higher relatively.

Table 9 Correlation of physico-chemical parameters in the bromate formation

		EC	F^-	pH	TA	TDS	TH	TU
Bromate	r- value	0.7680	0.5665	0.4989	0.7236	0.7542	0.2885	0.3702
	p-value	0.0000	0.0014	0.0059	0.0000	0.0000	0.1291	0.0481

Table9 Shows the Pearson’s correlation between physicochemical characteristics of water samples and the bromate concentration. According to Mindrila, D., & Balentyne, P. (2017) 0.7-1 strongly correlated, 0.5-0.7 moderately correlated and 0.3-0.5 low correlated. Due to this bromate was strongly correlated with electrical conductivity, total alkalinity and total dissolved solids. Whereas moderately correlated with fluoride, and PH; and also low correlated with total hardness and turbidity. As the ozonation treatment pH of the water is increased, the rate of bromate formation increases and also the presence of inorganic carbon (IC) species (alkalinity) increases bromate formation according to Jarvi *et al.*, (2007).

Table10: bromate value with water type and treatment

Brand code	Bromate value	Water type	Treatment
Bpw5	26.00±0.80^{b}	Mineral	Ozone and Nano filter
Bpw11	3.13±0.60^{a}	Natural purified	
Bpw29	4.20±1.70^{a}	Natural spring	
Bpw1	3.80±0.70^{a}	Mineral	Ozone
Bpw2	28.60±1.60^{g}	Mineral	
Bpw4	25.20±0.10^{f}	Mineral	
Bpw6	20.16±1.20^{e}	Natural	
Bpw7	4.70±0.50^{ab}	Natural purified	
Bpw8	32.60±0.88^{h}	Natural purified	
Bpw9	9.06±0.95^{c}	Natural purified	
Bpw13	BDL	Natural purified	
Bpw15	11.70±3.00^{d}	Natural purified	
Bpw17	3.70±1.70^{b-d}	Natural purified	
Bpw18	5.20±1.50^{c-e}	Natural purified	
Bpw19	4.06±1.20^{ab}	Natural purified	
Bpw22	2.40±0.00^{a}	Natural spring	
Bpw23	6.10±1.05^{b}	Natural spring	
Bpw25	6.50±2.00^{hi}	Natural spring	
Bpw26	6.00±1.30^{ef}	Natural spring	
Bpw27	5.50±0.70^{c-e}	Natural spring	
Bpw3	7.96±1.45^{c}	Mineral	Ozone and UV
Bpw10	4.46±1.05^{b}	Natural purified	
Bpw12	BDL	Natural purified	
Bpw14	BDL	Natural purified	
Bpw16	BDL	Natural purified	
Bpw20	9.16±1.35^{c}	Natural spring	
Bpw21	0.90±0.34^{a}	Natural spring	
Bpw24	11.10±0.50^{d}	Natural spring	
Bpw28	15.40±0.50^{e}	Natural spring	
Bpw30	5.50±1.50^{b}	Natural spring	

All the given values are means of three determinations ± standard deviation (SD), means in the same column with different superscripts are significantly different ($P < 0.05$) using Duncan’s multiple range test in Nano filter ,ozone treatment and UV treatment. All data are expressed as mean ± SD (n=3).

Table 10 shows that the bromate value in different water type and treatment value. Based on water type the concentration of bromate from five mineral water type three; from fourteen natural purified water two; from ten natural spring water two and one natural water type was higher bromate concentration. Bromate formation has been identified as a significant barrier in the application of ozone during water treatment for water sources that contain high levels of bromide according toWHO 2005, Jarvi *et al*, 2007. Whereas, the presence of bromide ions in waters treated with ozone can lead to bromate ions and brominated compounds formation, potentially carcinogenic. This poses a need to remove the bromates through other treatment, as UV Tammaro *et al*, 2016.And also removal of bromate and bromide by Nano filtration Lin *et al.*, 2020. But in the present study from three Nano treated samples one sample was higher bromate level. From seventeen sample treated by ozone was five samples higher bromate level. And also from ten samples treated by UV two samples have higher bromate level. But UV disinfection produces minimal DBPs (Peldszus *et al*., 2004). This result shows that the formation bromate was not only in the ozone treatment. According to Legube *et al*., 2004 increase in bromide inevitably leads to an increase in bromate for a constant ozone dose and contact time.

5. Conclusions and Recommendations

5.1. Conclusions

Packed water consumption was increase for drinking. As a result, in this study thirty brands of packed waters sold in Addis Ababa City, Ethiopia, were assessed for the level of bromate, fluoride, microbial load and Physico-chemical parameters of packed water. Based on the results of this study, in eight brands of packed water the bromate level was above the permissible limit. The bromate value of different packed brand waters samples from different water type were leveled and compared with the standard requirement and among themselves. But, in all samples was not bromate level on the label (packaged material).This research investigated that within three treatments and water type has bromate formation but not the all samples. This indicates that the treatment was not controlled. Bromate formation also positively strong correlated with pH, total alkalinity and electrical conductivity. The Ethiopian standard doesn't have the maximum required bromate value for packed brand water. But the WHO maximum permissible limit of bromate value was 10µg/L. The ability of maximum bromate concentration value in the drinking water to produce oxidative stress, resulting in damage to DNA, may play a role in its ability to induce renal tumors.

The fluoride level except ten brands of packed water all are not labeled on the label of the bottle (packaged).Therefore the remaining sample has not information about fluoride content. The other parameters (PH ,Electrical conductivity, total dissolved solid, total hardness, total alkalinity and turbidity) were fulfills the requirement as per the CES and WHO guide lines but in some brands the concentrations are far below the requirement and are not recommended for drinking as per WHO standards like PH and total hardness value.

Regarding to microbial parameter all brand packed water was suitable for human consumption according to WHO and CES standards.

5.2. Recommendations

- The study covers a limited number of branded packed waters, it is recommend that all marketed packed waters be monitored for treatment methods used, quality, safety and be licensed by the concerned authorities to safe consumers ‘health and ensure the sustainability. Finally, I recommend further studies should focus on:
- The possibility to verify the Ethiopian packed and municipal waters taking into account of increased number of samples and additional disinfection by products like TTHM’s and chlorite.
- For further study different treatment and occurrence of bromine during the process on the bromate reduction.

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7. Annex 1 Bromate by Colorimetry

The biological antiseptic quality of drinking waters is often maintained by the addition of oxidants. Ozone is a powerful disinfectant, effective in treating pathogens, and which oxidizes organic contaminants in much the same way as chlorine. Ozonation, however, tends to oxidize bromide to bromate, which presents a potential problem, since bromide is naturally present in spring waters. Bromate is a potential carcinogen, even at low microgram per litre (µg/L) level: a Maximum Admissible Concentration (MAC) of 10 µg/L bromate in drinking waters is recommended by the European Commission (in Directive 98/83), by the US EPA and the WHO. In addition, ozonation of surface (or mineralised) waters that contain natural bromide (or bromide impurities in added salts) can also result in the formation of bromate. The monitoring of bromate formation is important to verify the effectiveness of the treatment process.

Principle method: Bromate reacts with methylene blue solution in a hydrochloric acid medium. Methylene blue turns from blue in an oxidizing medium to colour less in a reducing medium, in relation to the concentration of bromate. The absorbance is measured photometrically at 665 nm.

Chemicals and materials

Items from manufacturers different from those on the list below may be used if they are shown to be functionally equivalent.

Chemical or reagent

- Hydrochloric acid **37 %** for analysis
- Potassium bromate for analysis or Sigma-Aldrich
- Methylene blue,
- Distilled or deionised water **without oxidizing agents and without bromate**

Materials

- Volumetric flask class A 50,100,500,and1000-mL
- Macropipette with adjustable volume, 0.5-mL – 5-mL and 1-mL – 10-mL)
- Tips for macropipette 5-mL and10-mL
- Plastic test-tubes with screw cap 25-mL
- Photometer Spectroquant® Prove 300 UK using 50 mm cells and capable of measuring absorbance at 665 nm
- Polyethylene containers 125,500,1000-mL
- 50 mm cell
- Funnels
- Balance accurate to 1 mg

7.1. Preparation of reagents

- 7.1.1. Stock solution of bromate 1 g/L
- Dissolve 130 mg ± 1 mg of potassium bromate with distilled or deionised water into a 100-mL volumetric flask. Dilute to 100 mL with distilled or deionised water.
- 7.1.2. Bromate solution 10 mg/L
- Pipette 1 mL of bromate stock solution 1000 mg/L (7.1.1) into a 100-mL volumetric flask. Adjust to 100 mL with distilled or deionised water. Mix well.
- 7.1.3. Bromate solution 1 mg/L
- Pipette 10 mL of bromate solution 10 mg/L (7.1.2) into a 100-mL volumetric flask. Dilute to 100 mL with distilled or deionised water. Mix well.
- 7.1.4. Bromate calibration solutions
- Pipette into a series of 500-mL volumetric flasks:
    - - 2.5 mL of bromate solution 1 mg/L (7.1.3)
    - - 5 mL of bromate solution 1 mg/L (7.1.3)

  - - 10 mL of bromate solution 1 mg/L (7.1.3)
  - - 1.5 mL of bromate solution 10 mg/L (7.1.2)
  - - 2 mL of bromate solution 10 mg/L (7.1.2)
- Adjust to 500 mL with the non-ozonated water sample without oxidizing agent and without bromate, or with distilled or deionised water.
- These calibration solutions contain (5 – 10 – 20 – 30 – 40) µg/L bromate respectively.
- 7.1.5. Bromate verification solutions
- 7.1.5.1. Bromate solution 10 µg/L
- This solution is used to check the calibration
- From a bromate solution 1 mg/L prepared as 7.1.3 but different from the stock solution used for the daily calibration, pipette 5 mL into a 500-mL volumetric flask. Adjust to 500 mL with the non-ozonated water sample without oxidizing agents and without bromate or with distilled or deionised water (see section 7.1.4).
- 7.1.5.2. Bromate reference solution 20 µg/L
- This solution is used to check the calibration
- Pipette 10 mL of bromate solution 1 mg/L prepared as 7.1.3 but not with the same potassium bromate (potassium bromate must come from another supplier) into a 500-mL volumetric flask. Adjust to 500 mL with the non-ozonated water sample without oxidizing agents and without bromate or with distilled or deionised water (see section 7.1.4).
- 7.1.6. Stock solution of methylene blue, 0.2 g/L
- Dissolve 200 mg of methylene blue with distilled or deionised water into a 1-L volumetric flask. Adjust to 1000 mL with distilled or deionised water. Mix well.
- 7.1.7. Dilute methylene blue solution, 0.02 g/L
- Pipette 10 mL methylene blue stock solution (7.1.6) into a 100-mL volumetric flask. Adjust to 100 mL with distilled or deionised water. Mix well before use.
- Wrap the bottle containing the solution in an aluminium foil to avoid direct sunlight to the solution.
- 7.1.8. Sampling procedure
- Representative samples provided for analysis must be clearly identified by their identification number, which must be reported along with the final analytical report.

8. Calibration

- Pipette 20 mL of each bromate calibration solution (7.1.4) respectively, into a series of 25-mL plastic test-tubes.
- Under a fume hood, add to each tube:
  - 1 mL methylene blue solution 0.02 g/L (7.1.8)
  - 1.5 mL hydrochloric acid 37 % (carefully)
- Close the test-tube with the cap and mix carefully.
- Set aside for 10 minutes at room temperature.
- Transfer the solution into a 50 mm cell.
- Select method at 665 nm and 50 mm cell (Spectroquant® Prove 300 UK).
- Report and record the absorbance of each calibration solution at 665 nm.
- Calculate the calibration curve, plotting absorbance against concentration (linear regression of the type Absorbance = [Slope x Concentration] + Intersect). Check the linearity of the regression (R^2 must be greater than 0.99).
- Check the calibration using a 10 µg/L ± 2 µg/L bromate solution (7.1.5.1) and a 20 µg/L ± 4 µg/L bromate reference solution (7.1.5.2),

  <u>Remark:</u>
- The cell must be clean and must always be introduced in the same way into the spectrophotometer.

9. Sample analysis

- Pipette 20 mL water sample into a 25-mL plastic test-tube.
- Under a fume hood, add:
  - 1 mL methylene blue solution 0.02 g/L (7.1.7)
  - 1.5 mL hydrochloric acid 37 % (carefully)
- Close the test-tube with the cap and mix carefully.
- Set aside for 10 minutes at room temperature.
- Transfer the solution into a 50 mm cell.
- Select method at 665 nm and 50 mm cell (Spectroquant® Prove 300 UK).

- Read the absorbance at 665 nm and determine the bromate concentration in the sample with the calibration curve.

Remarks:

- The cell must be clean and must always be introduced in the same way into the spectrophotometer.
- Use the same cell for calibration and sample measurement.

10. Calculations

Calculate the mass concentration, C, of bromate, in microgram per litre using the equation:

$$C = \frac{A - I}{S}$$

Where:

A = Sample absorbance value obtained from the spectrophotometer

I = Intersect value using calibration curve

S = Slope value using calibration curve

Example:

The equation of the calibration curve is:

$$y = -0.0036\,x + 0.7675$$

i.e. $A = -0.0036 \times C + 0.7675$

Where:

I = 0.7675

S = – 0.0036

The concentration is calculated using the formula:

$$C = \frac{A - 0.7675}{-0.0036} = \frac{-(A - 0.7675)}{0.0036}$$

$$C = \frac{0.7675 - A}{0.0036}$$

For an absorbance of 0.663, the bromate concentration is: $\frac{0.7675 - 0.663}{0.0036} = 29\ \mu g/L$

11. Expression of results

Bromate concentration values are expressed in µg/L, without decimals.

Results must be reported and filed with the corresponding calibration curve (plotted with EXCEL for example).

Flow chart

Preparation of reagents

↓

Sampling and preparation of test samples

↓

Calibration

↓

Sample analysis

↓

Calculations

↓

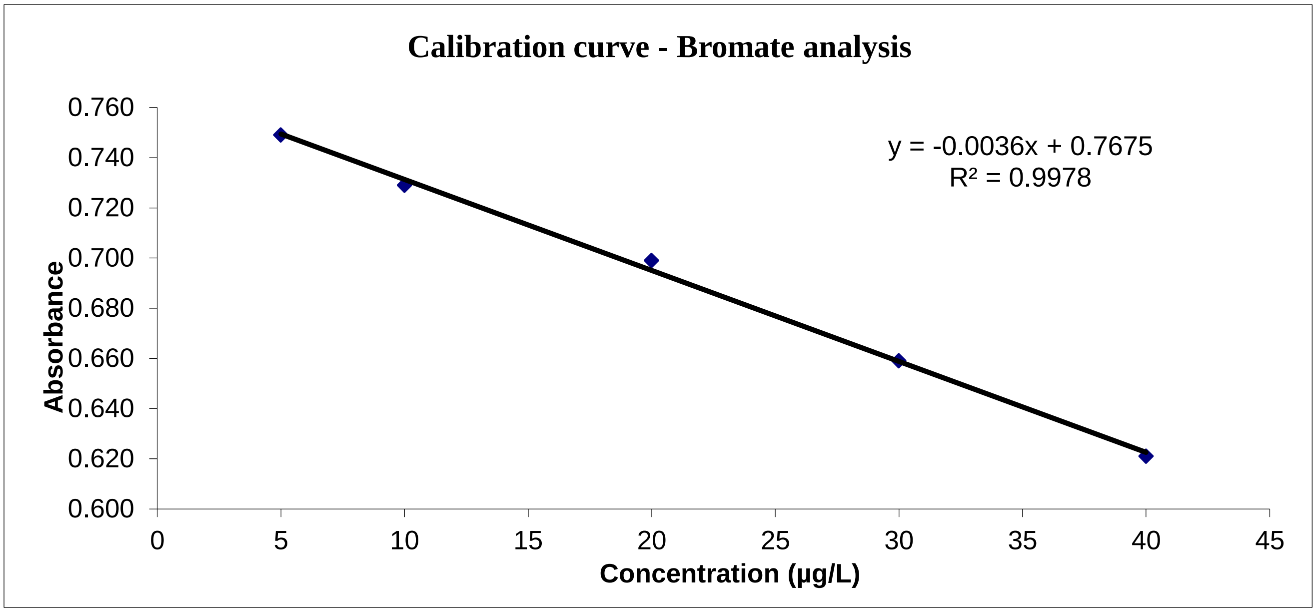
Expression of results

Example of calibration curve of bromate analysis (in distilled water) with NOVA 60 apparatus

A calibration curve (Graph 1) was plotted using the values in Table 2.

Table 1: Bromate concentration and optical density

Concentration (µg/L)	**Optical density at 665 nm**
5	0.749
10	0.729
20	0.699
30	0.659
40	0.621

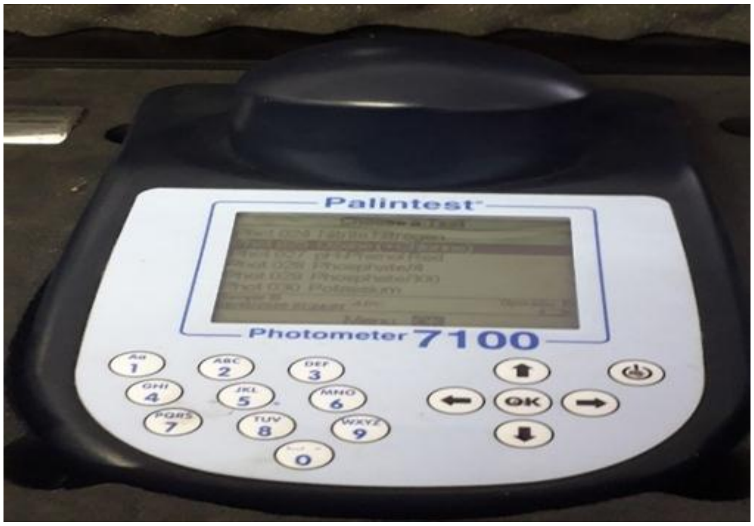


Graph 1: Example of bromate calibration curve (in distilled water) with NOVA 60

Titration for total hardness and Alkalinity

pH, EC and TDS meter

Turbidity meter

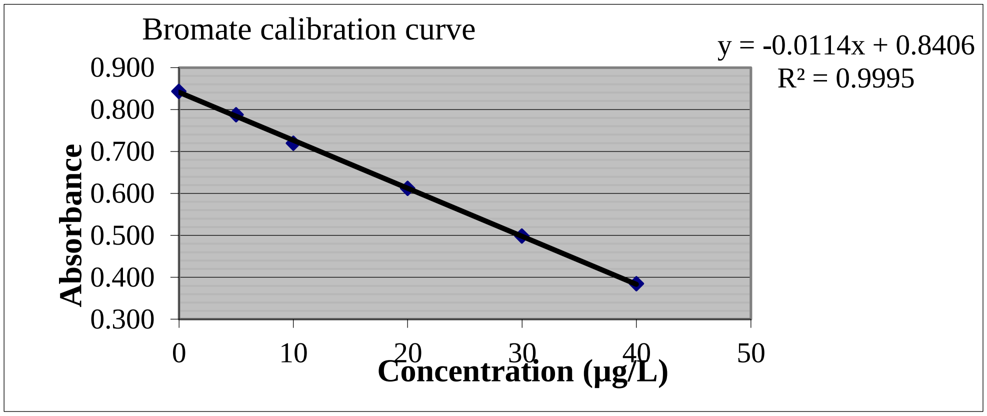


photometer 7100

UV/VIS Spectrophotometer

Concentration and absorbance of analysis for calibration

Concentration (µg/L)	**Absorbance**
0	0.843
5	0.787
10	0.719
20	0.612
30	0.498
40	0.385



Quality requirement for packed drinking water (CODEX STAN 108-1981, CES99 third edition 2019), and CES151, 2015).

Substance and Organism	**CES99**		**CES151**	
	Maximum permissible number	**Test method**	**Maximum permissible number**	**Test method**
Fluoride (as F), mg/L ,Max	1.5	ES ISO10359-1	1	ES ISO10359-1
Electrical conductivity µs/cm, max	1500	EISO7888	-	-
Total dissolved solids mg/L Max	1000	ES609	150-1500	ES609
PH value	6.5-8.5	ESISO10523	6.0-8.5	ESISO10523
Turbidity, max	5	ESISO7027	5	ESISO7027
Total Hardness (as $CaCO_3$) mg/I	300	ES607	400	ES607
Total alkalinity (as $CaCO_3$) mg/L, Max	600	ESISO9963-1	75-600	ESISO 9963-1
Coliform organism number per 100ml	undetectable	ES ISO 9308-1, ES ISO 9308-2	Undetectable	ES ISO 9308-1, ES ISO 9308-2
E. coli number per 100ml	undetectable	ES ISO 9308-1, ES ISO 9308-2	Undetectable	ES ISO 9308-1, ES ISO 9308-2
Fecal streptococci per 100ml	Undetectable	ES ISO 7899-1 or ES ISO7899-2	Undetectable	ES ISO 7899-1 or ES ISO7899-2
Total viable organisms colonies per 100ml	100	ES ISO 4833	100	ES ISO 4833