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« CHEMICAL QUALITY ASSESSMENT OF VARIOUS BOTTLED WATER MARKETED IN ALGERIA AND THEIR HEALTH-RELATED EFFECTS».

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Dedication

I dedicated this work for:

My beloved Mother

My Grandmother may God bless her soul

My family and friends; Rafika, her beloved mother, and all her family, Assia,

All the persons who loved me

List of Abbreviations & symbols

Abbreviations & symbols	Designation	Unity
APHA	American Public Health Association	
ATP	Adenosine 5’-triphosphate	
BGBL	Brilliant Green Bile Broth (medium)	
C	Concentration	
CVD	Cardiovascular diseases	
diam	diameter	
EPA	Environmental Protection Agency	
EDTA	Ethylene diamine tetra acetic acid and its sodium salts	
EC	Electrical conductivity	µc/cm
FAO	Food Agriculture Organization	
FDA	Food and Drug Administration	
JORA	Official Journal of Algerian Republic	
Litsky EVA	Ethyl-Violet-Azide-Litsky (medium)	
m	mass	g, mg
M	Mineralization	mg/L
mg	milligram	
NET	Eriochrome Black T indicator	
nm	nanometer	
PET	Polyethylene terephthalate	
pH	Potential of Hydrogen	
ppm	Parts per million	
T	Temperature	°C
TDS	Total Dissolved Solids	mg/L
T_2D	Diabete type 2	
TH	Total Hardness	mg/L
TGEA	Tryptone Glucose Yeast Extract Agar (medium)	
TSC	Tryptose sulfite cycloserine (medium)	
µs/cm	Micromhos per centimeter	
V	Volume	ml
WHO	World Health Organization	

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INTRODUCTION

I. INTRODUCTION

Water is essential for all abiotic and biotic processes on Earth,as component of both organic and inorganic substances as well as in its function as solvent (**Gordalla et *al.*, 2007**), reaction and transport medium.It has a number of unique chemical and physical properties that make it essential for life (**Gordalla et *al.*, 2007**), particularly safe drinking-water that guarantees significant health benefits; *World Health Organization* guidelines define safe drinking-water as it does not represent any significant risk to health over a lifetime of consumption (**WHO, 2017**). The water that is intended for human consumption must be free from chemical substances and micro-organisms in amounts which are universally accepted andthat would not produce a hazard to health.Supplies of drinking-water should not only be safe and free from dangers to health, but should also be as aesthetically attractive as possible through absence of turbidity, color as well as disagreeable or detectable tastes and odors is important in water-supplies intended for domestic use.

Water represents about 60% of the body weight of an adult human (**Gordalla et *al.*, 2007**), this percentage decrease gradually with aging. The presentwater in the living organism, ensures circulation, regulate blood pressure, enable absorption and the transportation of food, furthermore; influencing blood composition, thermoregulate elimination of metabolites maintains cellular osmotic pressure, and regulate the temperature of the body (**Marktl, 2009**).

People believes the idea that bottled water is healthy, because of its richness in minerals which confer health benefits (**Baba et *al.*, 2008; Ward et *al.*, 2009**). **Murakami et *al.***, (**2015**) proved in their study that serum glycol-albumin levels were significantly decreased after Bicarbonate Mineral Water consumption (*BMW*) it tends to lower blood sugar levels, which may prevent and/or improve type 2 Diabetes. Whilst, nitrate may have the effect of protecting the gastrointestinal tract from various gastrointestinal pathogens, because nitrous oxide and, acidified nitrite have antibacterial properties (**WHO, 2017**).

Also, potassium maintains the normal osmotic pressure in cells with sodium; it is a cofactor for many enzymes, a sufficient loss of potassium can result in

Hypocalcaemia, which causes: cardiac arrhythmia, muscle weakness, nausea, vomiting, and low muscle tone in the gut. Longer-term hypocalcaemia causes a predisposition to hypertension (**Udhayakumar et *al.*, 2016**). Wherefore Osteoporosis patients should select water with high calcium, and magnesium concentrations to help with their skeletal fragility (**Chiarenzelli & Pominville, 2008**).

Salt minerals are vital for human body as they can be toxic if consumption is excessive, and this may in some cases be baneful (**Stanhope, 2018**). Prolonged consumption of water with high EC (*Electrical conductivity*) and *TDS* (*Total Dissolved Solids*) may cause hypertension, heart attack, gastrointestinal irritation, and renal calculi (**Udhayakumar et *al.*, 2016; Rahman & Rahaman, 2018**).

Furthermore if serum calcium level rises to 160 *mg/L* may cause coma, and death; too high magnesium causes nausea, muscular weakness, and paralysis when it reads a level of about 400 *mg/L* (**Udhayakumar et *al.,* 2016**).

Therefore, patients with urinolithiasis issues can benefit from avoiding hard or mineralized waters. And those suffering from hypertension should monitor their sodium intake, and avoid waters with high sodium content (**Chiarenzelli &Pominville 2008**).

Excess in chlorine and sodium is harmful to people suffering from cardiac, circulatory, and kidney diseases. High sodium levels may cause hypertension with congestive heart failure (**Udhayakumar, 2016**).

Inorganic nitrate is the main contaminant in water, capable of causing acute toxicity problems; it may be a sign of other contaminants (**Fortunato et *al.*, 2020**). It is lately cancerous as reduction to nitrite can occur in the organism with primarily gastric cancers(**WHO, 2017**).

The ingestion of water that contains nitrate over 50 *mg/L* to 100 *mg/L* may give rise to infantile methaemoglobinaemia. (**WHO, 2017**), simultaneous gastrointestinal infections may alter human thyroid gland function by competitively inhibiting thyroidal iodide uptake, leading to altered thyroid hormone concentrations, and functions, (**Ward et *al.*, 2009; WHO 2017**) nitrate in water may also be related to the occurrence of childhood diabetes (**WHO 2017**).

Many studies were established to assess the quality of commercializedbottled water, and compare the results to the standards established by the current legislation (**Diduch et *al.*, 2011; Pontara, 2011**), bottled waters are still falsely labeled “mineral water”; in fact only about 30 of the more than 200 brands on the market in Poland deserve this name (**Diduch et *al.*, 2011**).

Consumers in Algeria always believe that bottled water is healthy and safe regardless of spring or mineral water. Mostly they are keen to take it with their medication during treatment, and whenever they can especially, for the elderly, pregnant women & children.

With all these facts, the consumer remains confused about choosing the best for his body, especially with the existence of many brands in the market.

According to the guide of mineral and spring water published by the Algerian ministry of trade in 2016, the number of bottled water processing units is forty-two, in operation (42 Brands between mineral, and spring waters), and thirty-one planned units.

The presentwork aims to control the quality of the bottled water soldin the Algerian market; the difference between mineral water and spring water;analyzing their major components; their conformity with the international and the local standards; and whether they pose a risk to the consumer’s health, along the following line:

- Bacteriological analysis: by analyzing the presence of the indicator bacteria such as: Aerobic mesophilic germs, coliforms groups, enterococci, anaerobic spores and *Pseudomonas aerugenosa.*
- Physicochemical analysis: the major componentswere analyzed, because of their stability to avoid the analytic incertitude related of sample(when concentration is high the incertitude is less). Basically, according to the parameters appear in its labels, such as: pH, dry residues, nitrate, calcium, magnesium, sodium,

potassium, bicarbonate, chloride and sulfate, and add some other parameters like: EC, TDS, salinity, hardness and organic matter

- Hydrochemical facies: by using Piper diagram and Durov diagram, to determine the water types.
- Comparethe results with the local and the international standards of drinking water.
- Classification of water samples into unknown groups depends on its chemical contents similarity, using Statistica software).

BIBLIOGRAPHIC STUDIES

1. Mineral and spring waters

Natural mineral water is microbiologically wholesome water from an underground aquifer tapped via one or more natural or drilled wells, near from where it conditioned (**JORA 45, 2004**). These natural mineral waters may have therapeutic properties favorable to human health (**JORA 45, JORA 51, FAO/WHO 1997**). The only treatment allowed prior to bottling is to remove unstable components such as iron and sulphides and to (re) introduce carbon dioxide.

According to the Codex Alimentarius, the natural mineral water is water clearly distinguishable from ordinary drinking water because:

a) It is characterized by its content of certain mineral salts and their relative proportions and the presence of trace elements or of other constituents.
b) It is obtained directly from natural or drilled sources from underground water bearing strata for which all possible precautions should be taken within the protected perimeters to avoid any pollution of, or external influence on, the chemical and physical qualities of natural mineral water.
c) Of the constancy of its composition and the stability of its discharge and its temperature, due account being taken of the cycles of minor natural fluctuations;
d) It is collected under conditions which guarantee the original microbiological purity and chemical composition of essential components.
e) It is package close to the point of emergence of the source with particular hygienic precautions.
f) It is not subjected to any treatment other than those permitted by this standard (**Codex Alimentarius, 108-1981**).

Natural mineral water is characterized by being in its original state as having been preserved intact because of the underground origin of the water thereby being protected from all risk of pollution.

The composition, temperature and other essential characteristics of natural mineral water must remain stable at source within the limits of natural fluctuation. An example of such is that they must not be affected by possible variations in the rate of flow.

Mineral water can be gaseous or non-gaseous. In terms of its treatment; disinfections are not allowed, filtration or decanting. The addition or removal of carbon dioxide is the only treatment authorized. Mineral water has to contain a minimum of 250 mg/l of minerals. However local standard differ per country.

Spring water is Water from a natural source that contains few minerals, In contrast to mineral water, which has to be bottled at the source; spring water may be transported first.

2. Genesis of water

The water was in the form of a hot vapor that stuck to tiny grains of rock which the aggregated to build up pebbles-an ultimately- a wet earth. Once the earth's crust began to solidify. It would have belched out huge quantities of water during a period of rampant volcanic eruptions, as the saturated atmosphere cooled. It began to rain-and rain-and rain, filling the earth's basins with the water that we inherit to this day (**Drake, 2005; Waller, 2008**).

Based on the position of these planets inside the water vapor cloud, earth has attracted more water vapor then the other planets (**DE Aquino, 2014**).

Water molecules have a simple structure: two hydrogen atoms bonded to one oxygen atom-H_2O- This simple structure is responsible for water's unique properties (see **Appendix 1**). The H-O-H bond angle in water is 104.3° (**Gordalla et *al.*, 2007**).

The reason for many of liquid water's special properties originates from the water molecules consisting of dipoles that associate through intermolecular hydrogen bonds in its condensed phase (see **figure 1**) (**Gordalla et *al.*, 2007**).

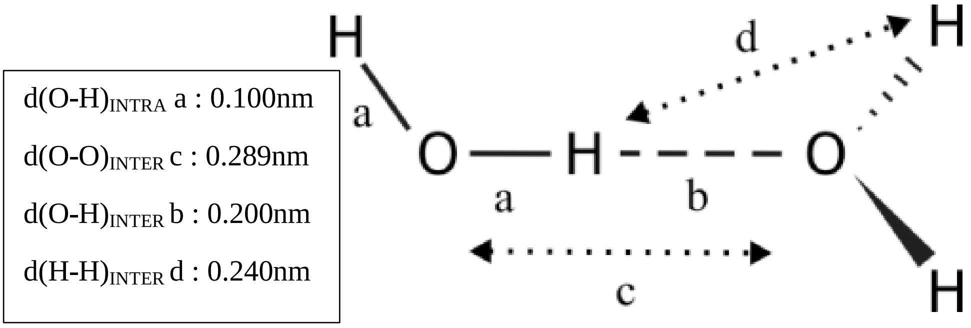


Figure 1: Geometry of the water molecule and energetically favored configuration of two molecules in condensed phase (Liquid) (**Gordalla et *al.*, 2007**).

3. Cycle of water

Another feature of water which is important for the hydrological cycle is its enthalpy of evaporation. Closely linked to this is the fugacity of water, which determines the amount of water that is converted into the gas phase and can be transported to the atmosphere (**Gordalla et *al.*, 2007**).

Due to its polar character, water is a good solvent for salts, polar organic compounds and gases. Within the hydrological cycle water directly interacts with various solid phases, such as dust, soil, rocks, and living organisms. As a consequence of ample contact between water and the atmosphere within the hydrological cycle. The components of the air, especially the gases nitrogen, oxygen, and carbon dioxide, will dissolve in water (**Gordalla et *al.*, 2007**).

4. Physicochemical characterizations of water

Due to its ability of forming intermolecular hydrogen bonds, water possesses a range of particular physicochemical properties which are of fundamental relevance for the matter and energy budgets of ecosystems.

Water with its formula H_2O , is the only inorganic compound that exists naturally on earth in all three physical states of matter-gas, liquid, and solid physical state under natural conditions, and it is always on the move among them. Pure water is colorless, odorless, and tasteless (**Gordalla et *al.*, 2007**).

The heat regulation of organisms depends on the high heat capacity of water. It contributes, for example, to the maintenance of a constant body temperature in warm-blooded organisms.

Water, being a strong dielectric, water's dielectric constant is one of the highest known for liquids is an excellent solvent for salts and gases, which are capable of solvolysis with subsequent dissociation (e.g. CO_2) (**Gordalla et *al.*, 2007**).

It dissolves a variety of substances very effectively. This is one of the reasons why almost all biochemical reactions take place in aqueous solutions and why water is indispensable as a reaction medium for all metabolic processes in living cells (**Gordalla, 2007**).

Natural waters are of widely diverse compositions depending upon their geologic and geographical origin (**WHO, 2017**).

5. Classification of mineral waters

Waters are differentiated by their chemical composition (quantity and nature of minerals contained in ionic form), temperature and pH (**Leeman, 2008; Richard, 1996**)

Natural mineral waters are classified in accordance to the geological, hydrogeological, physicochemical and microbiological criteria. Pharmacological, physiological, and clinical criteria are also considered if the natural properties of the water can be justified.

The mineral and chemical contents of bottled natural mineral water are determined by the composition of the rocks from which it is extracted and by geochemical processes (**Bartram & Pedley, 1996; Van der Aa, 2003**).

5.1. According to their composition

Mineral waters can be classify according of their composition, depends on the most dominant ion:

- Hardness: Soft, medium, highly mineralized;
- Sodium or calcium sulphide waters;
- Sulfated waters;
- Salinity; Sodium chloride water;
- Carbonated waters.etc. (**Van der Aa, 2003; Diduch, 2011**).

5.2. According to their temperature

Temperature is also a parameter of classification of mineral waters:

- Hyperthermale waters, where its temperature exceed to 50 °C ;
- Mesothermal waters or thermals, where the temperature located between 35 °C & 50 °C ;
- Hypo-thermal waters, where the temperature is between 20°C & 35°C ;
- Cold waters, where the temperature is lower than 20 °C (**Van der Aa, 2003; Diduch, 2011**).

5.3. Content of specific constituents

Mineral waters with special mineralization, which have high concentration of trace-elements. For example; ferruginous waters, when it contains more than 20 mg/L of iron.

6. Standards of drinking-water

Water can be admitted for consumption only when the concentration of its constituents does not exceed the norms.

When these norms can be established by nutritional standards and the highest permissible levels limiting values in the case of harmful or potentially toxic substances have been taken into account.

6.1.The Algerian standards of drinking-water

The aim of national drinking water laws and standards should be to ensure that the consumer enjoys safe potable water, not to shut down deficient water supplies. Effective control of drinking water quality is supported ideally by adequate legislation in each country will depend on national constitutional and other considerations.

Algerian legislation gave a big importance to follow the water quality from the exploitation sites and its conditions into the bottling process and quality control of the final products.

According to interminesterial Decree (**2016**), fixing the microbiological criteria of food. **Table 1** below shown all the indicator bacteria must be tested in mineral and spring water during the process of quality control.

Table 1: Bacteriological properties of mineral and spring waters.

category	Microorganisms/metabolites	Sampling plan		Microbiologic limits (ufc/g)	
		n	c	m	M
Mineral water and spring water	*Escherichia coli*	5	0	Absence in 250 ml	
	Enterococci	5	0	Absence in 250 ml	
	sulfite-reducing anaerobic spores	5	0	Absence in 250 ml	
	Total coliforms	5	0	Absence in 250 ml	
	Pseudomonas aerugenosa	5	0	Absence in 250 ml	

Where:

- **m:** number of germs present in one gram or milliliter of sample, which represent the value below which the water quality is considered to be satisfied;
- **n:** number of samples analyzed;
- **M:** number of germs present in one gram or milliliter of sample, which represent the value above which the water quality is considered to be unacceptable;

- **c:** maximum number of samples that may exceed "m" but below of "M" without rejected the batch.

The physicochemical quality is determined in the Executive Decree 2014, Relating to the quality of drinking water, the parameters and the indicative values shown below in **table 2**.

Table 2: Physicochemical parameters according to the Algerian executive Decree (**2014**).

Parameter group	Parameters	Unities	Limit values
Chemical parameters	Nitrate	mg/L	50
	Nitrite	mg/L	0.2
	arsenic	µg/L	10
	Plumb	µg/L	10
	Mercury	µg/L	6
Organoleptic parameters	Color	mg/L platine	15
	Turbidity	NTU	5
	Odor at 25°C	Dilution rate	4
	Taste at 25°C	Dilution rate	4
Physicochemical parameters relating with the natural structure of waters	Alkalinity	mg/L $CaCO_3$	65 minimum
	Calcium	mg/L	200
	Chloride	mg/L	500
	pH	/	$\geq$ 6.5 and $\leq$ 9
	Conductivity at 20°C	µS/cm	2800
	Total hardness	mg/L $CaCO_3$	500
	Total iron	mg/L	0.3
	Manganese	µg/L	50
	Phosphore	mg/L	5
	Potassium	mg/L	12
	Sodium	mg/L	200
	Sulfate	mg/L	400
	Temperature	°C	25

6.2.The international standards of drinking-water

The world health organization ken to keep up to date the guidelines for drinking-water quality, for primary purpose which is the protection of public health.

In microbiological quality the use of indicator organisms in monitoring is indicated, they must be absent in 100 ml (for *E.coli* and aerobic mesophilic count / heterotrophic plate count) (**WHO, 2017**).

Table 3 shown the chemical limit values in drinking water according WHO guidelines (**2017**).

Table 3: Guideline values for naturally occurring chemicals that are of health significance in drinking-water.

Chemical	Guideline value		Comment
	µl/L	mg/L	
Arsenic	10	0.01	
Fluoride	1500	1.5	
Mercury	6	0.006	
Cadmium	3	0.003	
Nitrate	50 000	50	
Nitrite	3 000	3	
Lead	10	0.01	
Copper	2000	2	
Chloride		250	
TH		500	No health-based guideline value
Sodium		200	No health-based guideline value
Sulfate		250	No health-based guideline value
TDS		600	No health-based guideline value
Turbidity		4 NTU	
Zinc		0.1	

Most chemicals arising in drinking water are of health concern only after extended exposure of years, rather than months, the principal exception is nitrate, which may cause methemoglobinemia.

In general the limit values in Algerian standards, whether microbiological or physicochemical parameters are inspired from the international norms of *WHO*, with some differences according to our local specificity.

7. Benefits of mineral waters

Hot spring water and natural mineral water are traditionally used in public baths and balneotherapy. In many countries, balneotherapy is the use of thermal and/or mineral water derived from natural springs or drilled water.

It used for the treatment of human health by employing various methods; such as bathing, drinking, mud therapy, and inhalation. This tradition founded in Arabic and Romanian civilizations (**AFFSA, 2008**).

Most countries recognize mineral waters as having properties of favorable to heath: in Germany this is called Heilwasser, this is -legally- considered a medicinal product. Their therapeutic effects are assigned to certain combination of dissolved compounds (**WHO, 2008**).

The medical importance of mineral waters depends on the contained amount of minerals and trace elements. The bioavailability of minerals from mineral water is good and can be compared with the values derived from milk.

A positive effect of the minerals in water on health status is especially apparent in the case of insufficient intake by nutrition (**Marktl, 2009**).

Certain constituents of drinking water may have adverse health effects. According to previous studies, it has been reported that balneotherapy has beneficial effects for various diseases; such as, type two diabetes (T_2D), rheumatism, low back pain and cardiovascular disease (**Murakami et *al.*, 2015**).

Recently the popularity of bottled mineral water with consumers has increased dramatically due to the ever-increasing contamination of water resources.

The mineral water industry has been very successful in marketing mineral waters as "better drinking water" for instance; the proportion of waterborne disease outbreaks linked by problems in public water distribution systems has been noted to be on the increase. These incidents convince the public to use bottled water.

Table 4 represents characteristics of the main natural mineral waters and their respective general therapeutic indications.

Table 4: Therapeutic indications of the main natural mineral waters.

Type of natural mineral water	Continent of the main mineral (mg/L)	Applications
Bicarbonate	>600 mg/L	Promote digestion, because neutralizes gastric acidity.
Sulfate	>200 mg/L	Lightly laxative; it is suggested for hepatobiliary diseases.
Chloride	>200 mg/L	Balance of intestine, bile ducts and liver; laxative effect.
Calcic	>150 mg/L	It is suggested for adolescents, pregnant women, subjects who don’t consume dairy products, elderly men; contributes to prevent osteoporosis and hypertension.
Magnesiac	>50 mg/L	Promote digestion
Fluorurate	>1 mg/L	Strengthen teeth structure and prevent dental decay; helps in osteoporosis.
Ferrous	>1 mg/L	It is suggested for anemia and iron deficiency.
Sodium-rich	>200 mg/L	It is suggested for intense physical activity (to replenish the salts leaked through sweating).
Low-Sodium	<20 mg/L	It is suggested in case of hypertension.

7.1. Effects of calcium and sodium

Sodium is present in mineral water but in small amounts only and mainly in the form of sodium bicarbonate which has no effect on blood pressure. A certain advantage of the delivery of minerals and trace elements by regularly drinking of mineral waters is the simultaneous intake of water without a supply of energy (**Marktl, 2009**).

If dietary sources also pose problems such as lactose intolerance, it may be advisable to prescribe certain specific waters, especially of the mineral kind with high calcium concentrations as a supplement (**Morr et *al*., 2006**).

The use of mineral water with high concentrations of calcium constitutes a calorie-free calcium source that can improve calcium supply. Adequate calcium Ca^{2+} intake is essential for normal growth and development of the skeleton and teeth as well as adequate bone mineralization (**Greupner et *al*., 2017**).

7.2. Effects of magnesium

An appropriate magnesium intake has proved to have cracked effects on bone health, reduces insulin resistance and prevents atherosclerosis (see **table 4**).

It acts as a stabilizer of the cell membrane by protecting the cell against sodium retention. There is a close relationship between the concentrations of potassium and magnesium both intracellular and extracellular.

Magnesium is an essential element for growth; it acts as a plastic element in bone and more than 50% of the body's magnesium (24g) belongs to the skeleton. It constitutes an activating element for the enzymatic systems (phosphatases, catalases, carboxylases), for the synthesis of proteins and for the metabolism of lipids.

Magnesic insufficiency leads to neuro-muscular disorders; the value of magnesium in the therapy of spasmophilia is well known. A magnesium deficiency can also result in cardiac manifestations, coronary lesions with arrhythmias (**Rodier et *al.*, 2009**).

Table 5 below presents minerals in some mineral waters and examples of their biological functions in human body (**Quattrini et *al.*, 2016**).

Table 5: Biological functions of some minerals present in water (**Quattrini et *al.*, 2016**).

Category	Mineral	Some biological Functions
Macronutrients	Calcium	Bone development, regulation of muscle contraction and myocardium activity, present in the human body blood clotting, nerve impulses transmission, regulation of cell permeability. in modest quantities
	Chlorine	Hydrochloric acid formation (digestive juices or digestion process).
	Phosphorus	Protein synthesis, ATP synthesis and transport of energy in biological systems.
	Magnesium	Bone formation, nervous and muscular activities, lipid metabolism and protein synthesis, CVD protection.
	Potassium	Muscles and myocardium activities, neuromuscular excitability, acid-base balance, water retention and osmotic pressure.
	Sodium	Fundamental regulation of cell permeability and body fluids; deficiency is rare, but an excessive intake may be associated with high blood pressure.
	Sulfate	Essential amino acids, cartilage, hair and nails formation, enzyme activity in redox processes and cellular respiration, intestinal peristalsis.
Micro-nutrients trace elements, essential for some biological	Cobalt	Constituent of vitamin B12: growth factor, nucleic acid synthesis, hematopoiesis.
	Chromium	Enzymatic reactions involved in the metabolism of carbohydrates, lipids and proteins.
	Iron	Blood and muscle tissues: hemoglobin, myoglobin.

functions	Fluoride	Protection and prevention of tooth decay, bone development; diseases related to excess.
	Iodium	Essential for the synthesis of hormones that are involved in the growth process and body development.
	Manganese	Synthesis of several enzymes involved in the metabolism of proteins and sugars, bone development.
	Molybdenum	Production of enzymes associated to uric acid.
	Copper	Functionality of several enzymes in blood and muscles
	Selenium	Protection of the muscle membrane integrity, antioxidant.

7.3. Effects of Bicarbonates

It has been suggested that drinking water may be an important source of mineral intake. Particularly the consumption of bicarbonate-rich mineral water has been reported to prevent or improve T_2D (**Murakami et *al.*, 2015**).

7.4. Effects Potassium

This element plays a role in the osmolarity of cells, and in the transmission of nerve impulse (**Rodier et *al.*, 2009**).

8. Chemical hazards in drinking-water

Epidemiological studies have examined the relation between exposure to trace elements (e.g. copper, zinc, arsenic, etc.), minerals (e.g. magnesium) and the occurrence of disease including reproductive outcomes.

Certain forms of cancer such as rare congenital mal-formations of the central nervous system, cardiovascular disease and sudden death. Due to waterborne minerals being in ionic forms and is easily absorbed into the gastrointestinal tract.

A number of chemical contaminants have been shown to cause adverse health effects in humans as a consequence of prolonged exposure through drinking-water. However, this is only a very small proportion of the chemicals that may reach drinking-water from various sources.

The ability of chemical constituents of water that can lead to health problems resulting from a single exposure, except through massive accidental contamination of a drinking water supply (**WHO, 2008**).

- **Calcium and sodium:** They are the dominant cations present in water; it may be due to the weathering of alkali feldspar in rocks. Their presence in high concentrations is harmful for patients suffering from cardiac, renal and circulatory diseases (**WHO, 2017**).

- **Chloride**: It is normally the most dominant anion in water, if it is exceed the permissible limit can be injurious to people suffering from heart and kidney diseases.

- **Magnesium**: It is directly related to hardness, too high magnesium causes nausea, mascular weakness and paralysis in human body when it reaches a level of about 400 mg/l (**Udayakumar et *al.*, 2016**).

- **Nitrate and nitrite**: Nitrate may arise from the excessive application of fertilizers or from leaching of wastewater of other organic wastes into surface water and groundwater. Nitrates are indirectly toxic in that they convert to nitrites; with regard to long-term toxicity. The danger of nitrates to human health is limited to some infants under one year of age. Nitrate in drinking water can cause methemoglobinemia, which is commonly known as “blue baby syndrome” (**Rodier et *al.*, 2009; WHO, 2017**).

- **Potassium**: At low doses, it does not present a significant risk. Moreover, since this element is under the control of homeostasis, even large variations in the content of the water would have only negligible effects on the concentrations of the body (**Rodier et *al.*, 2009)**.

- **Sulfate**: It can cause noticeable taste, and very high levels might cause a laxative effect in unaccustomed consumers (**WHO, 2008**).

- **Heavy metals**: Drinking arsenic-rich water over months and years causes arsenic to accumulate in the body. This can lead to arsenicosis. The effects of arsenicosis include skin problems cancers and vascular disease (**Gassambe, 2012**).

Excessive concentration of Fluor may cause; Fluorose dentaire, and several problems of teeth.

Lead is not an essential element for the human body, and its excess may cause Saturnisme, where the brain is the most sensitive organ.

Excess of mercury cause Hydrargyrism , which is ulcerations of the mouth, including loosening of teeth (**WHO, 2017**).

9. Bacterial hazards in drinking water

Infectious diseases caused by pathogenic bacteria, viruses and parasites (e.g. protozoa and helminths) are the most common and widespread health risk associated with drinking-water.

The public health burden is determined by the severity and incidence of the illnesses associated with pathogens, their infectivity and the population exposed. In vulnerable subpopulations, disease outcome may be more severe (**WHO, 2017**).

9.1.E.coli

It is considered one of the most suitable indicators of faecal contamination, it is a Gram-negative, facultative anaerobic, normally live in the intestines but if it exceed the limits that can lead to illnesses such as pneumonia, urinary tract infections, and diarrhea.

9.2.Total coliforms

It can originate from faecal contamination or from the environment. Coliforms which can occur naturally in soil, water and vegetation, indicate possible contamination from airborne sources or from product contact surfaces that have not been effectively disinfected. Coliforms are normally not present in natural mineral water sources. Therefore, they are considered as an indicator of contamination of the water at source or during the packaging process (**CAC/RCP 33-1985**).

9.3.Enterococci

They are a sub-group of faecal *Streptococci*. Compared to *E. coli* and coliforms they tend to survive longer in the water environment and are therefore used as an additional indicator of faecal contamination (**CAC/RCP 33-1985**).

9.4.Spore-forming sulphite-reducing anaerobes

The spores of this group of bacteria are very resistant towards various kinds of environmental stresses. Spore-forming sulphite-reducing anaerobes can originate from faecal contamination and due to the length of their survival in unfavorable environments; they are usually used as an indicator of faecal contamination (**CAC/RCP 33-1985**).

9.5.Pseudomonas aeruginosa

Pseudomonas aeruginosa is not a normal component of the natural flora of natural mineral waters. When detected, it is usually in low numbers but *Pseudomonas aeruginosa* can survive and grow in natural mineral waters. Therefore, its presence is considered as an indicator of contamination of the water at source or during the packaging process (**CAC/RCP 33-1985**). It is associated with eye and ear infections (**EPA, 2001**).

9.6.Aerobic mesophilic count / Heterotrophic plate count

The aerobic mesophilic count / heterotrophic plate count is part of the natural flora of natural mineral waters and is used as a process management indicator. A limited increase in the counts is normal from source to the packaging. Numbers increasing over a certain level can indicate deterioration in cleanliness, stagnation or development of biofilms (**CAC/RCP 33-1985**).

EXPERIMENTAL STUDIES

MATERIALS AND METHODS

1. MATERIALS AND METHODS

- The bacteriological and the physicochemical analyzes carried out in the accredited laboratory, LRF-Djelfa.
- **Sampling**

42 different brands of spring water and mineral water samples were purchased from various markets in Algeria (see **table 6**). They were sold in its original packaging, PET (polyethylene terephthalate), three samples from each brand.

The brand name, manufacturing and expiry dates, batch number, the chemical contents and the address of manufacture were documented in proforma. The water samples were coded and stored in the dark at room temperature and quickly analyzed in the laboratory.

The water samples were analyzed just after its opening first for its bacteriological quality then for its chemical contents; five repetitions for each parameter were used to estimate the uncertainty in measurement (see **Appendix 3**). The analyses were achieved according to **APHA** (**2017**) & **Rodier et *al.*** (**2009**) methods. **Figure 2** shown the diagram of experimental protocol.

Table 6: Bottled water brands purchased to be analyzed.

N°	Spring waters	Mineral water
01	*Ain Bouglez*	*Lalla khadidja*
02	*Hassia*	*Texanna*
03	*Tazliza*	*Guedila*
04	*El Ghadir*	*Ifri*
05	*Ouwis*	*Alma*
06	*Lajdar*	*Lavita*
07	*Righia*	*ElGoléa*
08	*Fezguia*	*Salsabil*
09	*Mileza*	*Saida*
10	*Nestle Pure life*	*Baniane*
11	*Togi*	*Mouzaia*
12	*Ovitale*	*Thevest*
13	*Bir-Essalam*	*Toudja*
14	*Soummam*	*Messerghine*
15	*arwa*	*Youkous*
16	*Mont Djurdjura*	*Manbaa el ghezlane*
17	*Ifren*	
18	*Ayris*	
19	*Star*	
20	*Guerioune*	
21	*Besbassa*	
22	*Sidi Rached*	
23	*El Kantara*	
24	*Djebel Amour*	
25	*Taya*	
26	*Messad*	

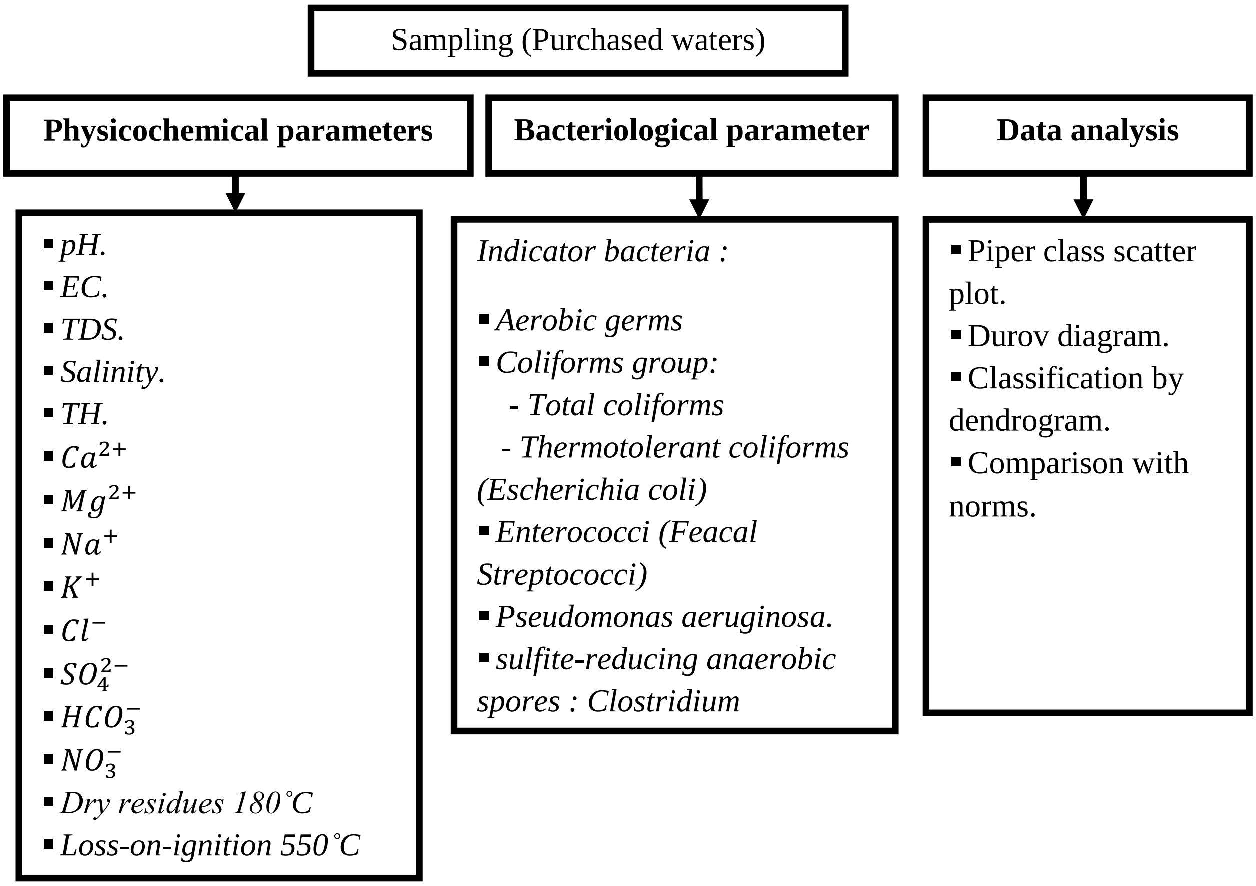


Figure 2: The experimental protocol diagram.

1.1. Bacteriological analysis

The under groundwater is naturally protected from the contamination of pathogenic bacteria, but there are many microorganisms in surface water. The contamination of spring and mineral water can happen during bottling. The bacteriological quality measured by the indicator organisms (**APHA 2017; Pontara, 2011)** in particular: Total coliforms, *Escherichia coli*, *Pseudomonas aeruginosa*, *enterococci*, and sulfite-reducing anaerobic spores: *Clostridium perfringens* and *Aerobic germs*, using the membrane filtration method, Horizontal method and multiple fermentation tube technique.

The media used in the analysis provided by Conda pronadisa. They were prepared and sterilized just before the analysis, with all the glassworks, using autoclave (Systec VE65). Also the workplace sterilized, and Bunsen burners were placed to allow us working inside the sterilization zone (20cm, diam.) around the Bunsen fire. Microbiological incubators (BINDER) were used to incubate tubes and Petri dishes, an electronic colony counter used to enumerate the bacteria colonies.

1.1.1. Mesophilic Aerobic microorganisms

Mesophilic aerobic germs are bacteria, yeasts or molds (**Ettel et *al.*, 2000**), which form colonies under the conditions defined according to the procedure shown in **figure 3** (**Rodier et *al.*, 2009; APHA 2017**).

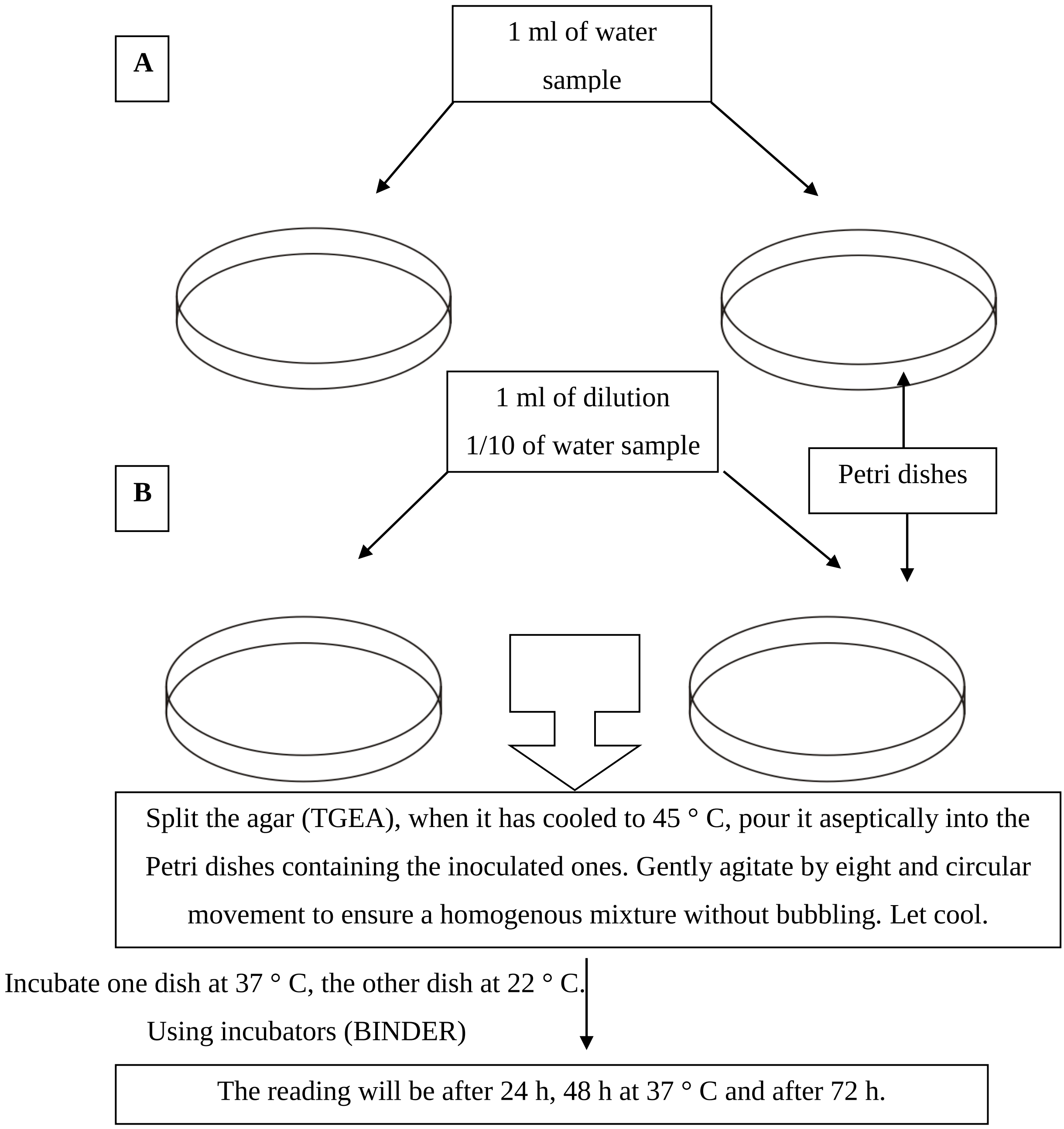


Figure 3: Procedure for the enumeration of Aerobic mesophilic.

1.1.2. Membrane filter technique for *Pseudomonas aeruginosa*

Filtration ramp system with 6 positions was used for the analysis, and cetrimide agar as selective medium for *Pseudomonas aeroginosa*.

Procedure:

- Dispense 5 ml portions of sterile medium (Cetrimide) into 50×9 mm Petri dishes, then let solidify at room temperature.
- Filter appropriate volume (250ml) through a sterile membrane filter 47-mm, 0.45μm pore-diam, and gridded membrane under partial vacuum.
- Place each membrane on a poured petri dish, rolling from one side to the other so air bubbles are not trapped under it (no air space between the membrane and the agar surface).
- Invert petri dishes; place the Petri dishes in close-fitting box or plastic bag containing moistened paper towels. Incubate them at least 24±2h at 37°C.

Pseudomonas aeroginosa produces a yellowish to green diffusible pigment (**APHA 2017**).

1.1.3. Multiple-tube fermentation technique for members of the Coliforms group

Total coliforms appear as Gram negative bacilli, non-sporogenic, non-pathogenic, oxidase negative, facultative aero-anaerobes. The most common genera of coliforms are Escherichia, Enterobacteriaceae, Citrobacterium, Serratia, and Klebsiella, with *Escherichia coli* being most abundant in the intestines of humans and other warm-blooded animals. They are identified by their ability to ferment lactose with the production of acids and gas, in 24 to 48 hours at 37 ° C (**Leclerc, 1996; Chigbu & Sobolev, 2007**).

Thermotolerant Coliforms (Feacal coliforms) are a subgroup of total coliforms consisting mainly of *Escherichia coli*, Enterobacterium, and some Klebsiella. They inhabit the intestines of warm-blooded animals, since they can grow and ferment lactose at a relatively high temperature (45°C) to produce gas, so they have been called "thermo-tolerant coliforms" (**Leclerc, 1996**). The high number of thermotolerant coliforms in the water is considered to be indicative of feacal contamination (**Chigbu & Sobolev, 2007**).

Procedure

- Presumption test: Arrange fermentation tubes in rows of five /ten each in a test tube rack.
- Use the fermentation technique with 10 replicate tubes each containing 10 ml, 5 replicate tubes each containing 20 ml, and a single bottle containing 100 ml sample portion.
- Promptly incubate inoculated tubes and bottles at 37°C (Using BINDER incubators).
- After 24 h±2h swirl each tube or bottle gently examine it for growth, gas, and acidic reaction (shade or yellow color) and if no gas or acidic reaction is evident, re-incubate and re-examine at the end of 48 h±3h.
- Process all tubes or bottles demonstrating growth with or without a positive acidic or gas reaction, through the confirmed phase (**APHA, 2017; Richard, 1996; Rodier, 2009**).

The procedure of searching and counting total and thermotolerant coliforms is shown schematically in **figure 4**.

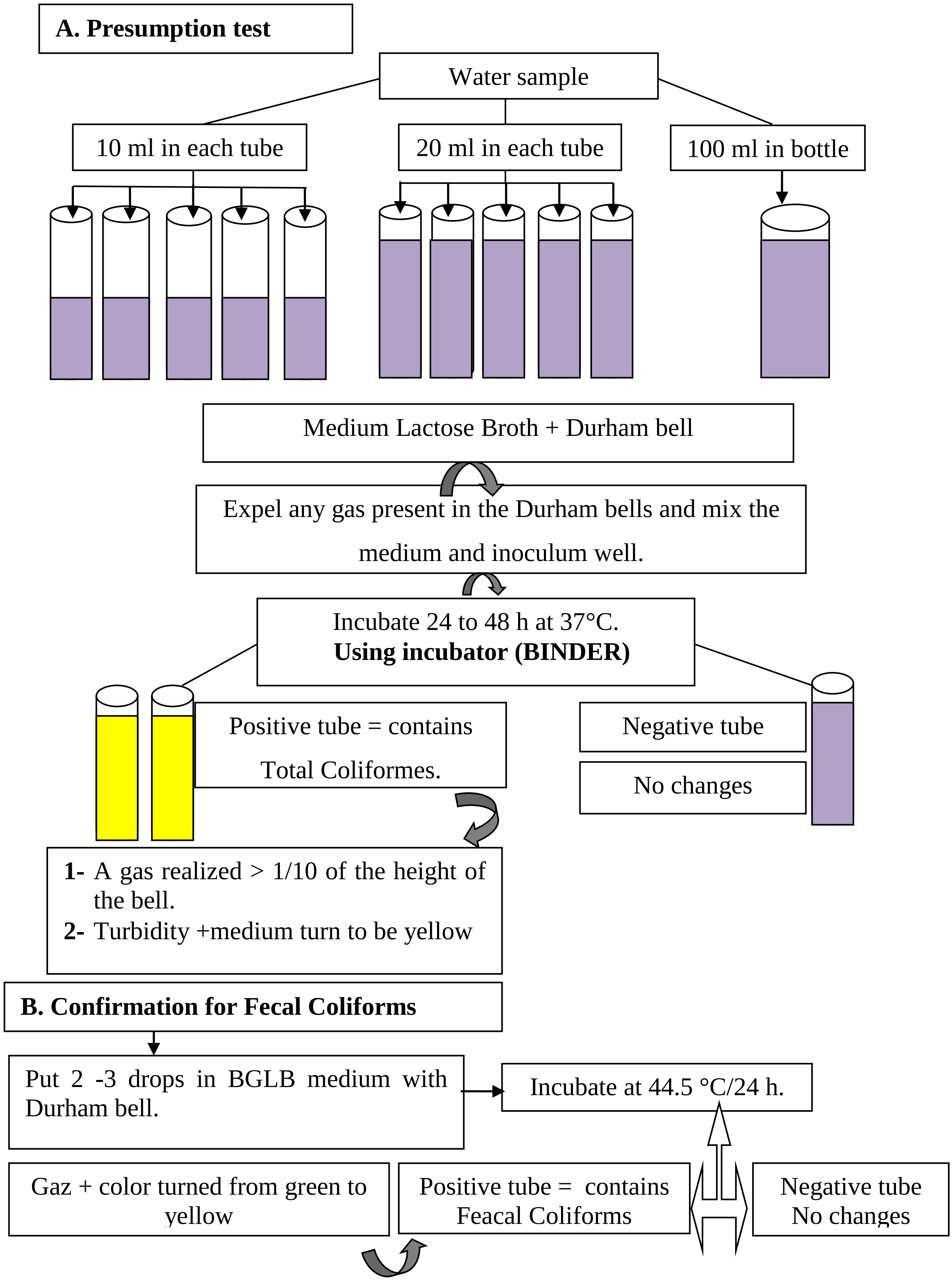


Figure 4: Procedure for the enumeration of Coliforms group.

1.1.4. Enumeration of sulfite-reducing Clostridium

This methodology is used for strict anaerobic Gram-positive bacilli microorganisms characterized by the resistance of their spores and by enzymatic equipment that reduces sulphites to sulphides.

These spores can survive in water and the environment for several months. The procedure for the search and enumeration of sulfite-reducing Clostridium is shown schematically in **figure 5**. (**AFNOR NF V 08-019/ISO 7937, 1985; Rodier, 2009; APHA, 2007**).

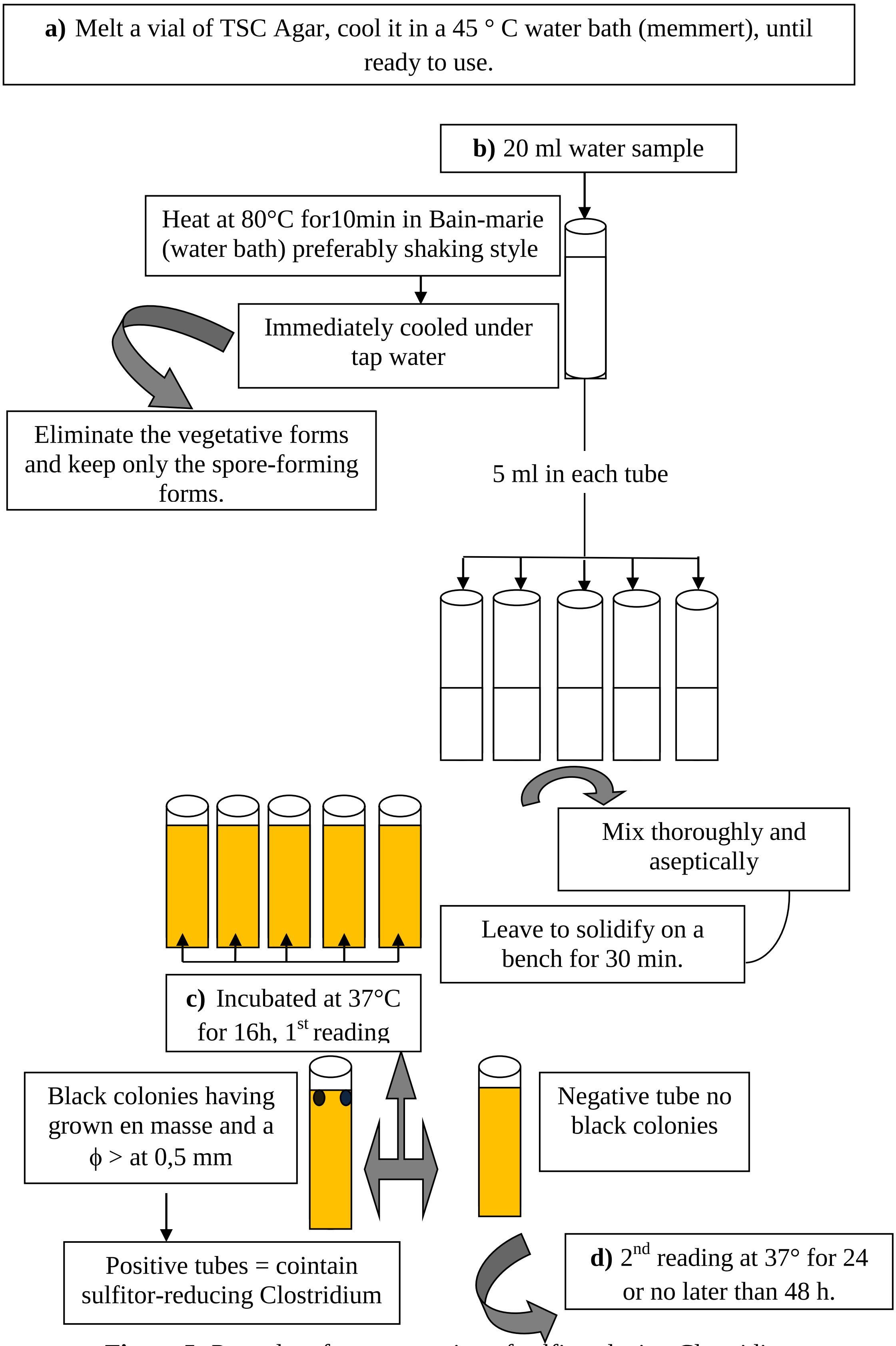


Figure 5: Procedure for enumeration of sulfit-reducing Clostridium.

1.1.5. Detection of Enterococci (faecal *Streptococci*)

They are Gram positive and also tend to live longer in water than fecal coliforms. They have been used as indicators of faecal contamination in water contamination (**Chigbu & Sobolev, 2007**). The group includes many species of bacteria in the genus Streptococcus such as, *S. faecalis*, *S. bovis*, *S. equines*, *S. avium*, *S. faceium*, and *S. gallinarum*, which are normally found in tailings and intestine of warm-blooded animals' contamination (**Chigbu & Sobolev, 2007**).

Procedure

- Presumption test: inoculate a series of tubes of Roth medium D/C with appropriate graduated quantities of 10ml, 1ml, and 0.1ml.
- Incubate inoculated tubes at 37°C for 24±2h, examine each tube for turbidity at the end of 24h.
- If no define turbidity is present, re-incubate, and read again at the end of 48±3h.
- After 48 h, subject all tubes showing turbidity to the confirmed test for enterococci (**APHA 2017**).

The procedure for the detection and enumeration of enterococci (faecal streptococci) is shown schematically in **figure 6**.

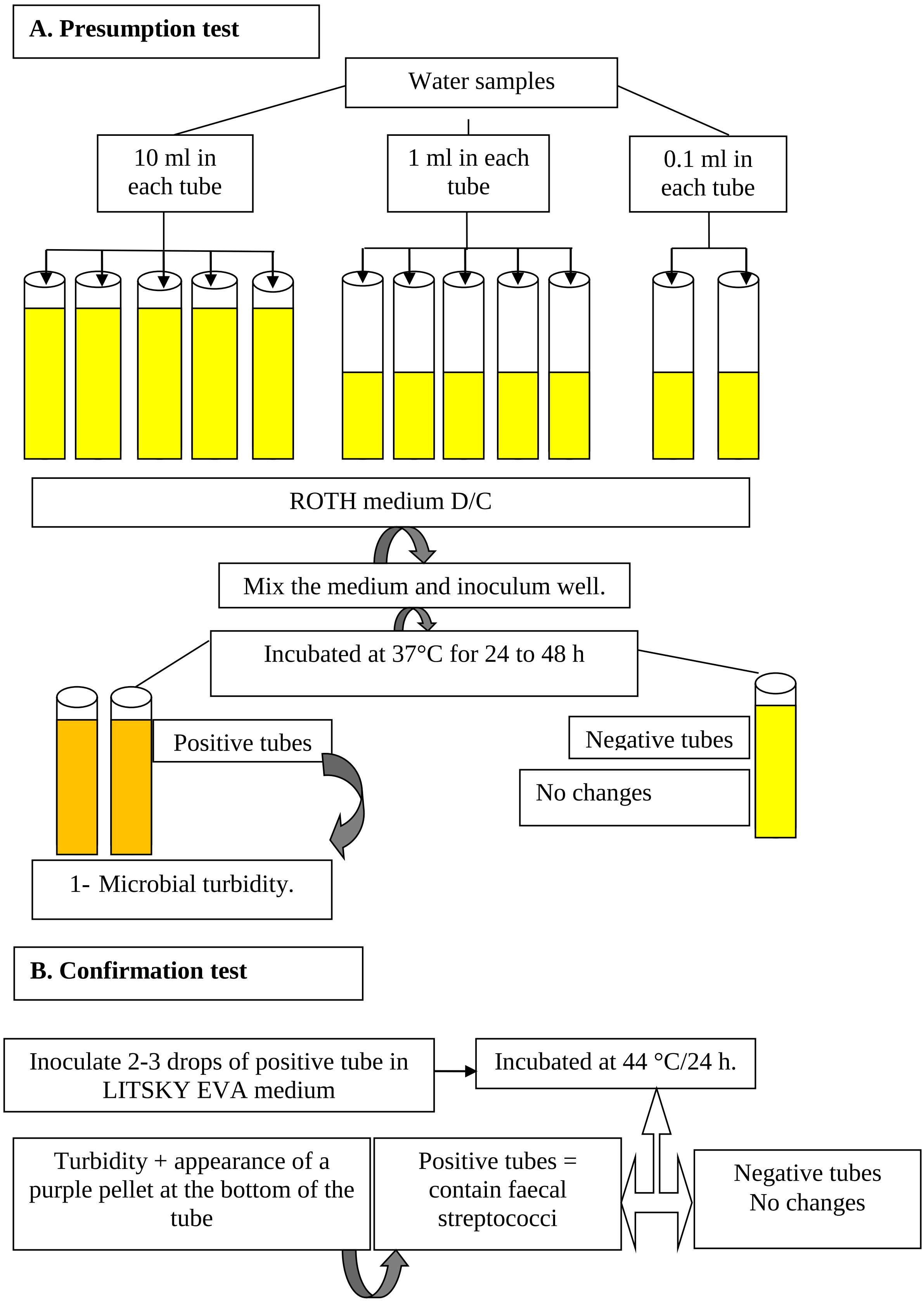


Figure 6: Procedure for detection and enumeration of Enterococci (faecal Streptococci).

1.2.Physicochemical analysis

1.2.1. pH

The measurement of pH is one of the most important and frequently used tests in water chemistry. This parameter measures the concentration of H^+ protons in water, and therefore the acidity or alkalinity of water on a logarithmic scale from 0 to 14. It influences most of the chemical and biological mechanisms in water. Usually, pH values are between 6.5 and 8.5 in natural waters (**APHA 2017; Derwich et *al.*, 2010**). The pH is measured directly by the pH meter (HACH, sens pH3).

Procedure

- Before use, remove electrode from storage solution, rinse, blot dry with a soft tissue.
- Calibrated with pH 4.0, pH 7, and pH 10 buffer solutions. Repeat (rinse, blot dry with a soft tissue) after each measurement.
- Stir gently the sample, put the electrode inside, then read the pH.

1.2.2. Electric Conductivity (EC)

Conductivity is a measure of the ability of water to conduct an electric current, therefore an indirect measure of the ionic content of water. It is expressed in micro Siemens per centimeter (μs/cm) (**Derwich et *al.*, 2010; APHA, 2017**). The conductivity is measured directly by the conductivity meter (HACH, sens ION^{TM}+EC7) (calibrated with 12.88 ms/cm, 1413 us/cm and 147 um/cm).

1.2.3. Dissolved salts (Mineralization)

Total Dissolved solids are represent the total concentration of substances dissolved in water. TDS is composed of inorganic salts and some organic matter. Common inorganic salts found in water include calcium, magnesium, potassium, and sodium which are all cations and carbonates, nitrates, bicarbonates, chlorides, and sulfates which are all anions. Mineral water springs contain water with a high level of dissolved solids because they have flowed through areas where the rocks contain a lot of salt. It represents the mineralization when the organic matter neglected.

There is a relationship between the content of dissolved salts in water and its conductivity. Estimate TDS (mg/L) in a sample by multiplying conductivity (in micromhos per centimeter) by an empirical factor:

If the electric conductivity (EC) between 333 and 833 µs / cm: M (mg / l) = 0.715920 × EC.

If the electric conductivity C between 833 and 10,000 µs / cm: M (mg / l) = 0.758544 × EC (**Rodier et *al.*, 2009; APHA, 2017**).

1.2.4. Salinity (S)

The salinity of the water is much more due to salt formations such as gypsum, it is influenced by the lithology of the water table and climatic factors (precipitation and temperatures). It measured directly by conductivity meter (mg/L).

1.2.5. Total hardness (TH)

The hardness of water results from the presence of divalent cations, especially calcium (Ca^{2+}), and magnesium (Mg^{2+}). From an ecological point of view, fresh water is more sensitive to biological and chemical phenomena likely to modify its pH (**Cotrovo et *al.*, 2010; Derwich et *al.*, 2010**). Titration is used to determine total hardness (**Tabouche & Achour, 2004**).

Use the EDTA tirimetric method, measures the calcium and magnesium ions, small amount of a dye (Erichrome Black T) is added to the water sample (the aqueous solution containing calcium and magnesium at pH= 10.0+ 0.1.

The solution becomes red if EDTA is added as titrant the calcium and magnesium will be complexing the solution turned, and when all of the calcium and magnesium has been complexing the solution turns from red to blue, marking the endpoint of the titration (**APHA, 2017**). The procedure is shown in **figure 7**.

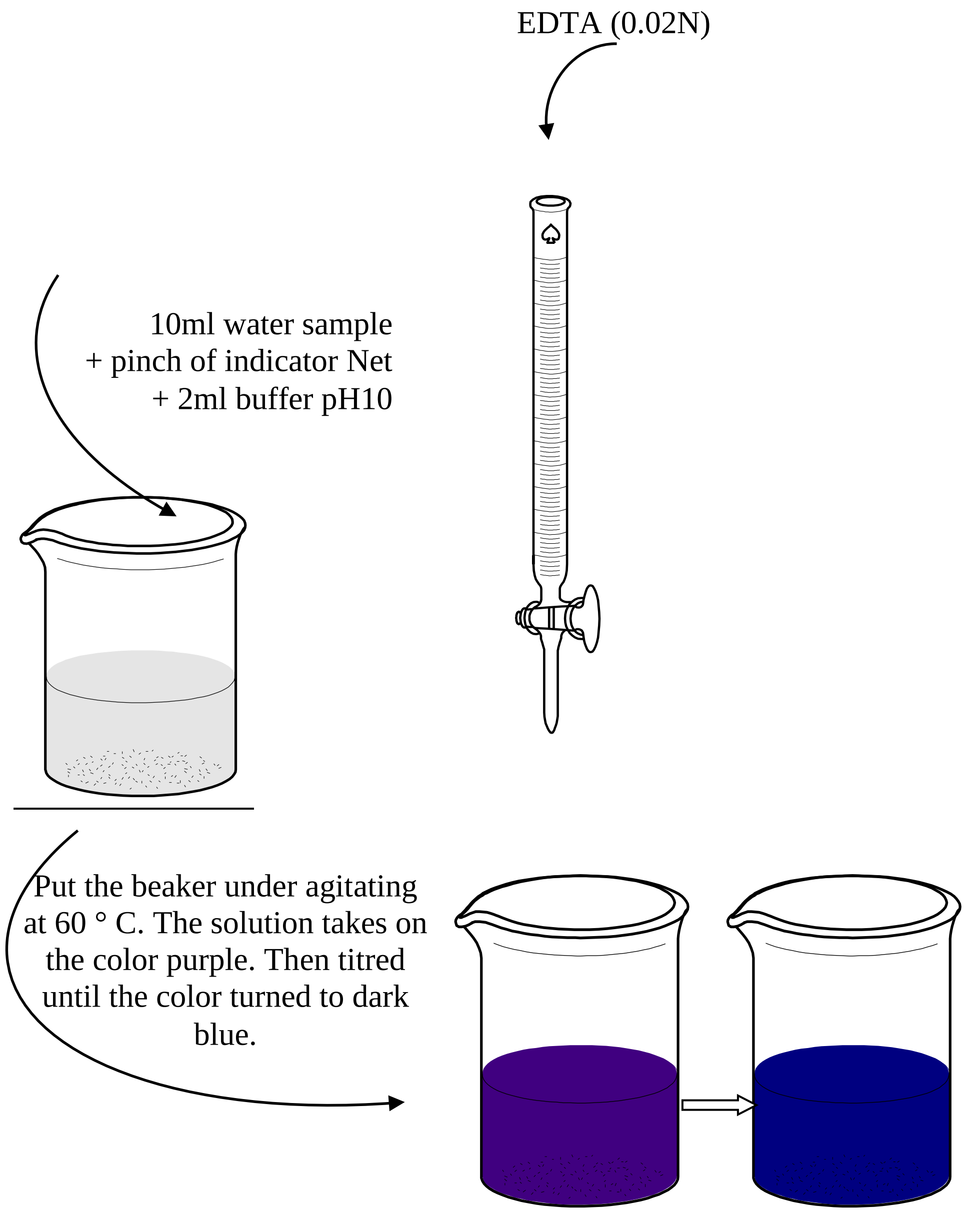


Figure 7: The determination of (TH) by Titration.

The hardness is calculated according to the following equation:

$$\mathbf{TH\ m\acute{e}q/l} = \frac{\mathbf{(V \times N)EDTA \times 1000}}{\mathbf{V\ water\ sample}}$$

1.2.6. Determination of calcium Ca^{2+}

The principle of calcium dosage is identical to that of total hardness. However, since the assay is done at high pH (**Richard, 1996; Tabouche & Achour, 2010**), magnesium is precipitated as hydroxide and is not involved. Moreover, the chosen indicator only combines with calcium, the titration is carried out. According to the operating mode shown schematically in **figure 8**.

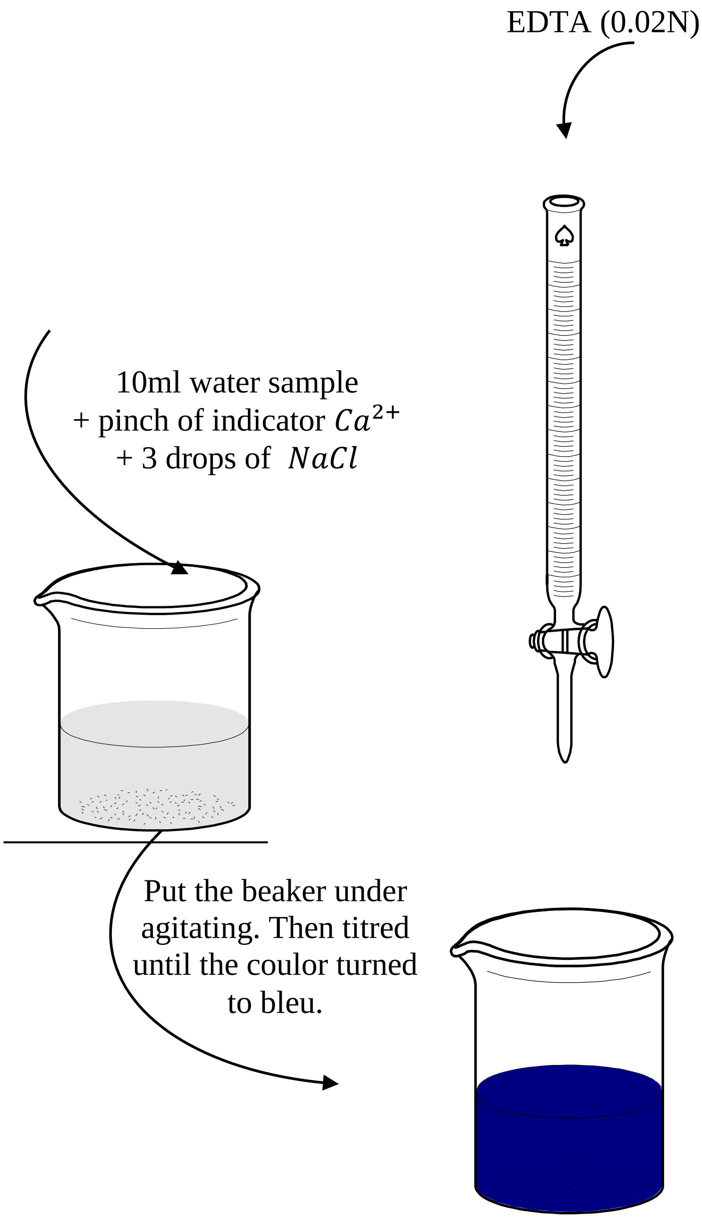


Figure 8: Calcium assay by EDTA titrimetric method.

We calculate the concentration of Ca^{2+} according to the following equation:

$$Ca^{2+}\ \mathbf{méq/l} = \frac{\mathbf{(N \times V)EDTA \times 1000}}{\mathbf{V\ water\ sample}}$$

$$Ca^{2+}\ \mathbf{mg/L} = \left[\frac{\mathbf{(N \times V)EDTA \times 1000}}{\mathbf{V\ water\ sample}}\right] \times \frac{\boldsymbol{MCa^{2+}}}{\boldsymbol{e}}$$

Où : M Ca^{2+}= 40.08 g/mol, e = 2 (**Rodier et *al.*, 2009**).

Also used flame photometer to measure the calcium concentration **§ 1.2.8**.

1.2.7. Determination of Magnesium $\boldsymbol{Mg^{2+}}$

It is an essential element in red cell blood. Concentration greater than 125mg/L also can have a cathartic and diuretic acid.

The magnesium may be estimated as the difference between hardness and calcium as $CaCO_3$, using the following relation:

$$\boldsymbol{Mg^{2+}}\ \mathbf{méq/l} = \mathbf{TH} - \boldsymbol{Ca^{2+}}$$

$$\boldsymbol{Mg^{2+}}\mathbf{mg/l} = [\mathbf{TH} - \boldsymbol{Ca^{2+}}] \times \frac{\boldsymbol{MMg^{2+}}}{\boldsymbol{e}}$$

Où : M $\boldsymbol{Mg^{2+}}$ = 24.36 g/mol, e = 2 (**Rodier et *al.*, 2009, APHA 2017**).

1.2.8. Determination of $\boldsymbol{Ca^{2+}}$, $\boldsymbol{K^{+}}$ and $\boldsymbol{Na^{+}}$ by Flame photometer

The potassium is an essential element in human nutrition, and occurs in groundwater as a result of mineral dissolution, from decomposing plant material, and from agricultural runoff.

The Sodium it is very soluble, it is important in human physiology; in large concentration it may affect persons with cardiac difficulties. A limiting concentration of 2 to 3 mg/L is recommended in feed waters destined for high-pressure boilers.

Using low temperature, single channel emission flame photometer JENWAY (see **figure 9**) designed for the routine determination of sodium and potassium. Additional filters are available for the determination of lithium, calcium and barium.

Figure 9: Flame photometer JENWAY PFP7.

Principle

Flame photometry relies upon the fact that the compounds of the alkali and alkaline earth metals can be thermally dissociated in a flame and that some of the atoms produced will be further excited to a higher energy level.

When these atoms return to the ground state they emit radiation which lies mainly in the visible region of the spectrum. Each element will emit radiation at a wavelength specific for that element. The measure emission intensity change automatically when the filter select turned to the main element (K^+ =766.5nm, Na^+= 589nm) (**APHA 2017; Manual PFP7**).

Procedure

For each element, it needed to prepare calibration curves using standards, according to their limit of detection:

$\boldsymbol{Na^{+}}$**:** 0.2 ppm, top concentration 10 ppm;

$\boldsymbol{K^{+}}$**:** 0.2 ppm, top concentration 10 ppm and,

$\boldsymbol{Ca^{2+}}$**:** 15 ppm, top concentration 100 ppm.

- Prepare the standards, five measurements from zero to the top concentration.
- Set the filter select control to the desired position. Aspirate distilled Water to adjust the 0 ppm, by adjusting the blank control.
- Aspirate the standard solution of slightly higher concentration than expected in the samples to be tested.
- Adjust the fine and coarse control until a positive reading is obtained, the reading taken at 20 seconds intervals.
- Use pre-diluted sample if the concentration is higher than the top concentration of the element (**Manual PFP7**).
- Read directly the concentration by ppm on the screen, and taking in consideration the dilution factor if used.

1.2.9. Determination of Chloride $\boldsymbol{Cl^{-}}$

One of the major inorganic anions in water. Some waters containing 250 mg/L may have a detectable salty taste if the cation is sodium.

Argentometric method is used to determine the concentration of chloride in water, in a neutral or slightly alkaline solution; potassium chromate can indicate the endpoint of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed (**APHA, 2017**). A titrating solution of silver nitrate is reacted in a neutral medium on a known test portion of standard sodium chloride solution. According to the operating mode shown schematically in **figure 10**. The reaction takes place in the presence of potassium chromate:

$$\boldsymbol{AgNO_3} + \boldsymbol{NaCl} \longrightarrow \{\boldsymbol{Ag\,Cl}\} + \boldsymbol{Na\,NO_3}$$

$$\boldsymbol{2Ag\,Cl} + \boldsymbol{K_2CrO_4} \longrightarrow \boldsymbol{2K\,Cl} + \boldsymbol{Ag_2CrO_4}$$

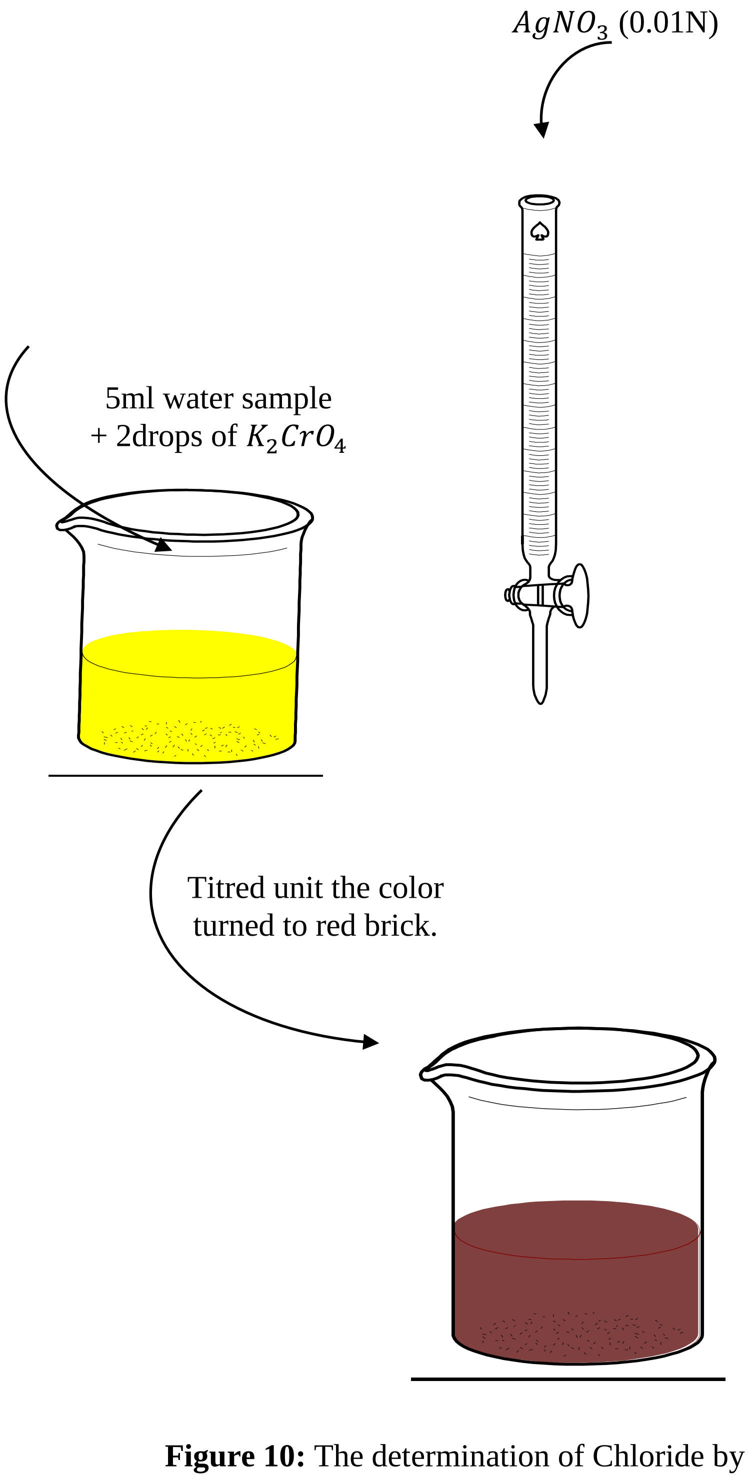


Figure 10: The determination of Chloride by Titration.

The concentration of Cl^- is calculated according to the following equation:

$$\boldsymbol{Cl^-}\ \mathbf{mg/l} = \mathbf{V}(\boldsymbol{AgNO_3})\ \times\ \mathbf{71}\ \times\ \mathbf{F}$$

Where: F is the correction of the $\boldsymbol{AgNO_3}$ titer , F $= \frac{1}{VAgNO_3}$

1.2.10. Determination of alkalinity HCO_3^-

For the assay, note the pH of the water to be analyzed, then titrate with HCl at 0.1 N until a pH of 4.4 is obtained, if the pH of the water is greater than 8.3, titrate up to this value then continues the dosage until pH 4.4 (**Rodier et *al.*, 2009; APHA, 2017**). According to the operating mode below in **figure 11**:

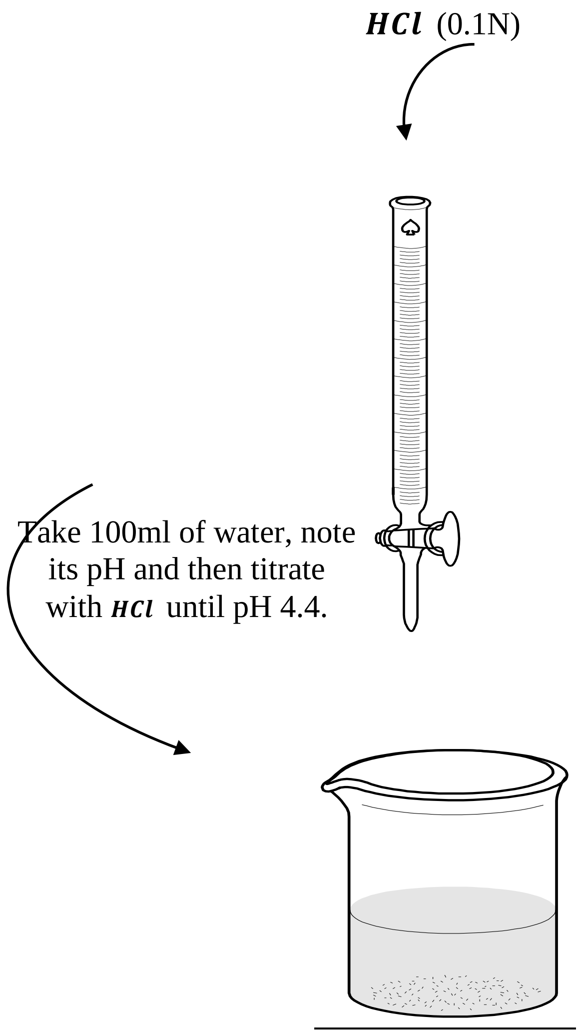


Figure 11: The dosage of HCO_3^-.

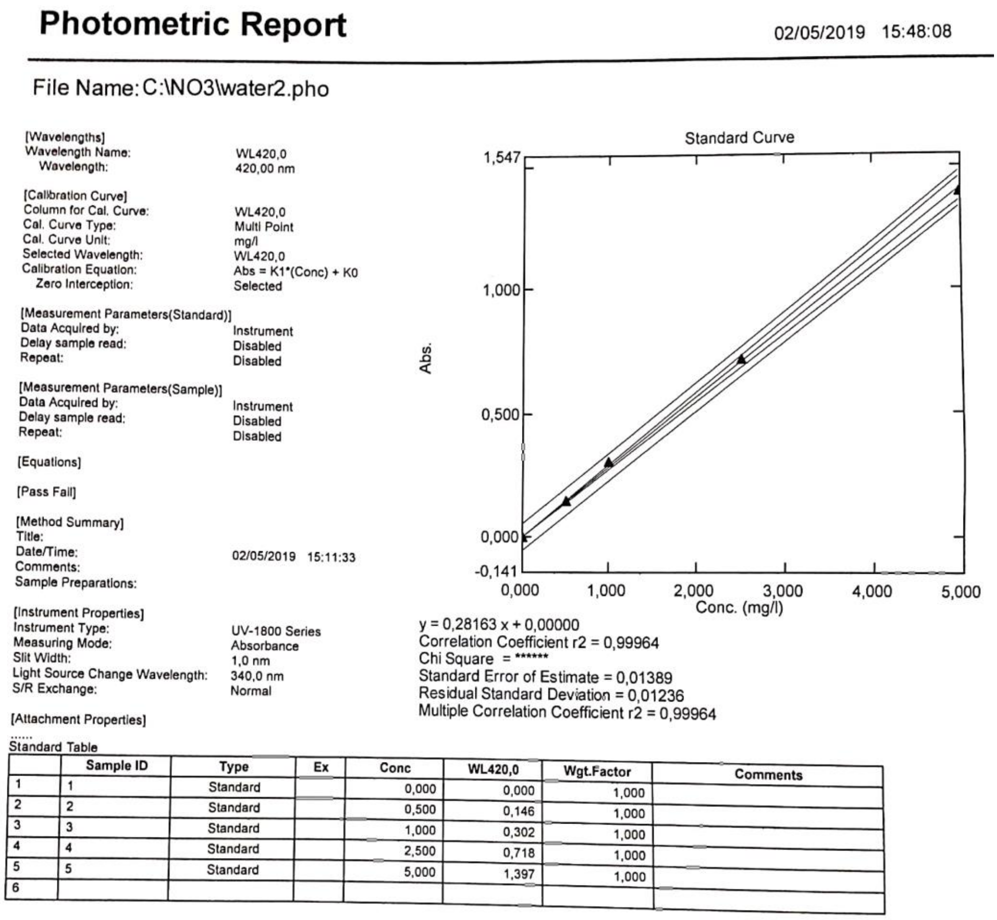
We use the following relation:

$$HCO_3^- \mathrm{mg/l} = \mathrm{V} \times 61$$

V: Volume of acid poured.

1.2.11. Determination of nitrate NO_3^-

The sodium salicylate method is used to determine nitrate. A calibration curve of NO_3^- prepared in the range 0 to 5 mg NO_3^- : 0mg/L, 0.5mg/L, 1mg/L, 2.5mg/L, and 5mg/L. The standard curve shown in **figure 12** used to measure the nitrate concentrations, by UV-Visible spectrophotometer (SHIMADZU UV-1800).



Photometric Report 02/05/2019 15:48:08

File Name: C:\NO3\water2.pho

[Wavelengths]
Wavelength Name: WL420,0
Wavelength: 420,00 nm

[Calibration Curve]
Column for Cal. Curve: WL420,0
Cal. Curve Type: Multi Point
Cal. Curve Unit: mg/l
Selected Wavelength: WL420,0
Calibration Equation: Abs = K1*(Conc) + K0
Zero Interception: Selected

[Measurement Parameters(Standard)]
Data Acquired by: Instrument
Delay sample read: Disabled
Repeat: Disabled

[Measurement Parameters(Sample)]
Data Acquired by: Instrument
Delay sample read: Disabled
Repeat: Disabled

[Equations]

[Pass Fail]

[Method Summary]
Title:
Date/Time: 02/05/2019 15:11:33
Comments:
Sample Preparations:

[Instrument Properties]
Instrument Type: UV-1800 Series
Measuring Mode: Absorbance
Slit Width: 1,0 nm
Light Source Change Wavelength: 340,0 nm
S/R Exchange: Normal

[Attachment Properties]
......

y = 0,28163 x + 0,00000
Correlation Coefficient r2 = 0,99964
Chi Square = ******
Standard Error of Estimate = 0,01389
Residual Standard Deviation = 0,01236
Multiple Correlation Coefficient r2 = 0,99964

Standard Table

	Sample ID	Type	Ex	Conc	WL420,0	Wgt.Factor	Comments
1	1	Standard		0,000	0,000	1,000	
2	2	Standard		0,500	0,146	1,000	
3	3	Standard		1,000	0,302	1,000	
4	4	Standard		2,500	0,718	1,000	
5	5	Standard		5,000	1,397	1,000	
6							

Figure 12: Calibration curve prepared to analyze nitrate in water samples.

Procedure

- In glass dish put 10 ml of the sample plus two drops of 30% $NaOH$ ml and 1 ml of sodium salicylate.
- Evaporated in a water bath 75-88 ° C then allowed to cool.

- Take up the residue with 2 ml H_2SO_3 , after 10 min 15ml of distilled water is added, add 15ml of double tartrate.
- Then pass through a spectrophotometer at a wavelength of 420 nm (**Rodier et *al.,* 2009**).

$$[NO_3^-] \text{ méq/l } = \text{reading} \times \text{ dilution}$$

$$[NO_3^-] \text{ mg/l} = [NO_3^- - \text{ méq/l}] \times \frac{MNO_3^-}{e}$$

1.2.12. Determination of sulfate SO_4^{2-}

The presence of sulfates in water is linked to the dissolution of gypsum. Sulfate ion is precipitated in an acetic acid medium with barium chloride so as to form barium sulfate crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer and the sulfate concentration is determined by comparison of the reading with a standard curve (**Rodier et *al.,* 2009**).

Procedure

- Preparing a calibration curve in range from 0 to 40 mg SO_4^{2-} .
- **Formation of barium sulfate turbidity:** Measure 100 ml of sample in Erlenmeyer flask, add 20 ml buffer solution and mix in stirring apparatus, while stirring add spoonful of $BaCl_2$ crystal and begin timing immediately. Stir for 60±2s at constant speed.
- **Measurement of barium sulfate turbidity:** After stirring period has ended. Pour solution into absorption cell of photometer and measure turbidity at 5±0.5 min (**APHA 2017**).

- Read it at (λ = 420nm) by UV-Visible spectrophotometer (SHIMADZU UV-1800). Using the equation below:

$$SO_4^{2-} \text{méq/l } = \text{reading} \times \text{ dilution}$$

$$\boldsymbol{SO_4^{2-}}\ \mathbf{mg/l} = \left[\,\boldsymbol{SO_4^{2-}}\ \mathbf{m\acute{e}q/l}\right] \times \frac{\boldsymbol{M\,SO_4^{2-}}}{\boldsymbol{e}}$$

1.2.13. Determination of the dry residues at 180°C

The determination of residues makes it possible to estimate the content of dissolved and suspended matter in water, according to the following steps:

- Stir or mix sample through, use a pipet or graduated cylinder to transfer a measured volume to a pre-weighed dish.
- Evaporated it to dryness at 180°C±2°C using an oven (BINDER 300°) repeat the cycle (drying, cooling, desiccating and weighing) until the weigh change is < 0.5mg (constant weight).
- Leave to cool for 15 min in the desiccator, and weigh immediately and quickly.

Calculation:

$$\mathbf{Dry\ Residues}\ \ (\mathbf{180°})\ \mathbf{mg\backslash l}\ \ = \frac{(\,\mathbf{m1 - m2})\ \times\ \mathbf{1000}}{\mathbf{V}}$$

- m1: The mass of empty dish (g).
- m2: The mass of the dish after drying (g) (4 hours at T = 180°C).
- V: Sample volume (ml) (**Rodier et *al.*, 2009; APHA, 2017**).

1.2.14. Loss on ignition at 550°C

Fixed and volatile solids ignited at 550°C: the residue from dryness is ignited to constant weight at 550°C±25°C, it gives the amount of organic matter present in water.

- Bring a muffle furnace (Nabertherm B180) to 550°C±25°C.
- Insert a dish containing residue produced by **§ 1.2.13** or sample into furnace.
- Ignite for at least 4 hours, cool in desiccator to ambient temperature, and weight, repeat the cycle (igniting, cooling, desiccating and weighing) until the weigh change is < 0.5mg (constant weight).

Calculation:

$$\text{Loss on ignition } (550°)\ \text{mg}\backslash\text{l} = \frac{(\text{m1} - \text{m2}) \times 1000}{\text{V}}$$

- m1: The mass of empty dish (g).
- m2: The mass of the dish after drying (g) (4 hours at T = 550°C).
- V: Sample volume (ml) (**Rodier et *al.*, 2009; APHA, 2017**).

1.3. DATA ANALYSIS

1.3.1. Hydrogeochemical study

The physicochemical data were studied by graphic treatment with Piper class scatter plot, to assess the origin and hydrochemical process of waters (**Piper, 1944; Fantong et *al.*, 2015; Kut et *al.*, 2018**), and Durov plot.

Grapher software version 17 was used to plot these diagrams for better understanding of samples' hydrogeochemical quality.

A. Piper diagram

Piper diagram is a multifaceted plot where in milliequivalents percentage concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and anions (HCO_3^-, SO_4^{2-}, and Cl^-) are plotted in two triangular fields, which were then projected further into the central diamond field (see **figure 13**).

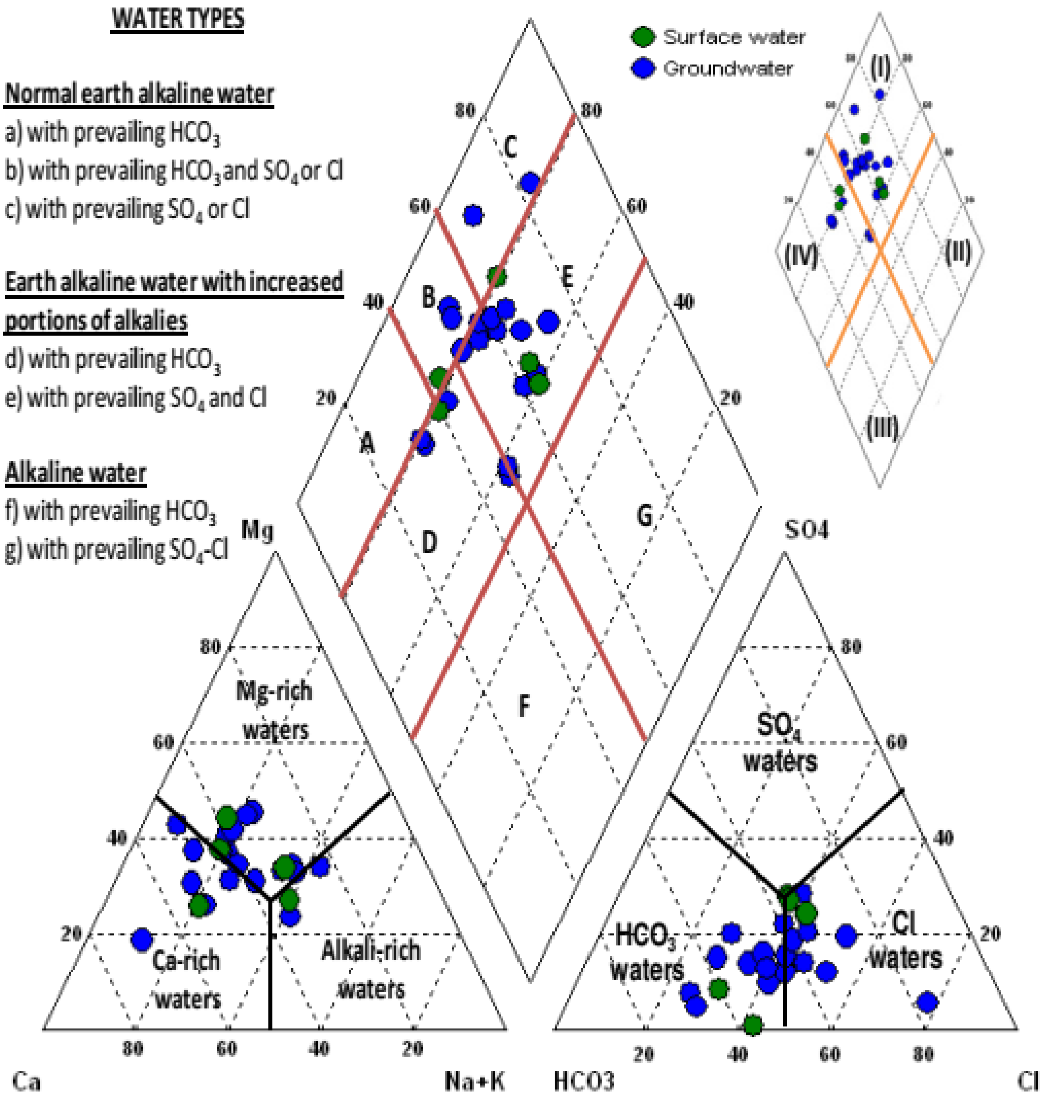


Figure 13: Piper trilinear diagram classifying major hydrochemical facies (Languth, 1966 *In* **Ravikumar et *al.*, 2015**).

B. Durov diagram

Durov diagram is a composite plot consisting of 2 ternary diagrams where the milliequivalents percentages of the cations of interest were plotted against that of anions of interest; sides form a central rectangular, binary plot of total cation vs. total anion concentrations (see **figure 14**). The classification of water based on Durov diagram shown in **table 7**.

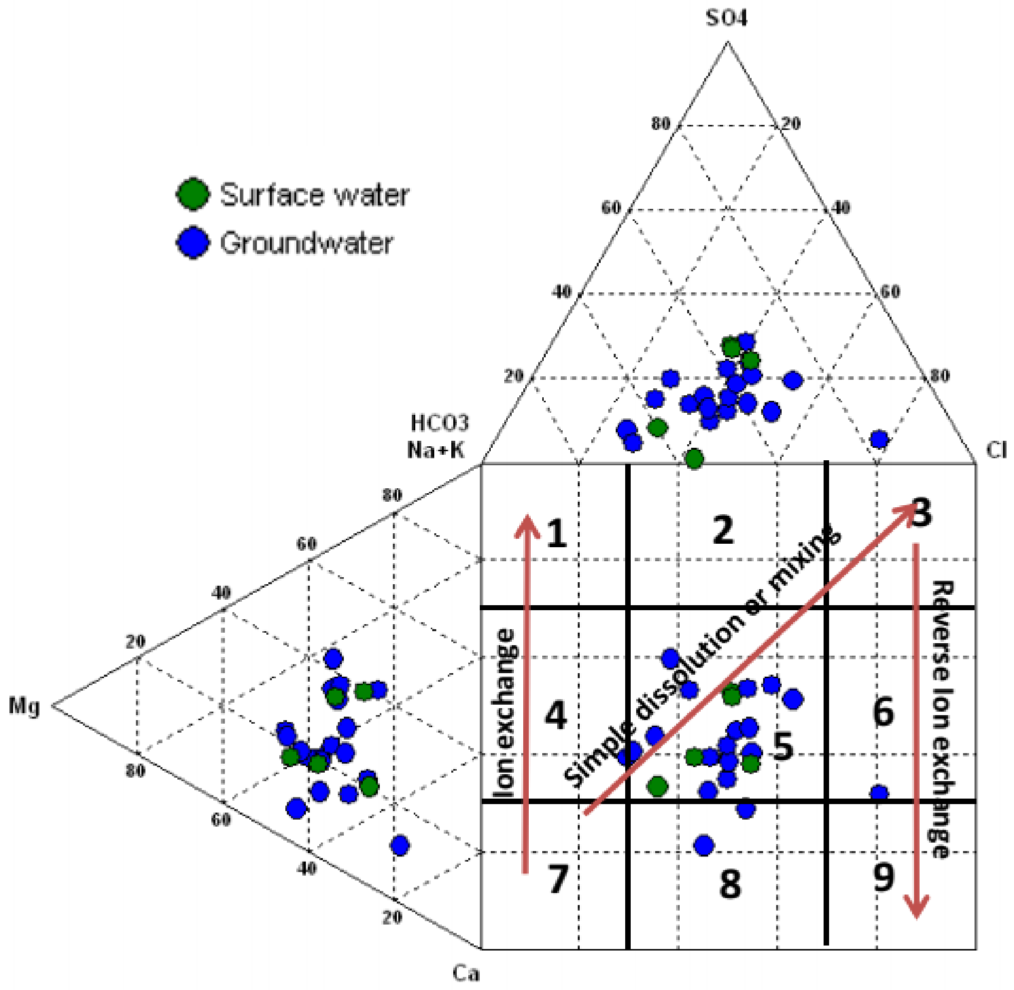


Figure 14: Durov diagram depicting hydrochemical facies (**Lloyd & Heathcoat, 1985** *In* **RAVIKUMAR et *al.*, 2015**).

Table 7: Classification of water based on Durov diagram (**Lloyd & Heathcoat, 1985** *In* **Ravikumar et *al.*, 2015**).

Field number	**Water types**
1	HCO_3^- and Ca^{2+}, dominant, frequently indicates recharging waters in limestone, sandstone, and many other aquifers
2	This water type is dominated by Ca^{2+}, and HCO_3^- ions. Association with dolomite is presumed if Mg^{2+}, is significant. However, those samples in which Na^+ is significant, an important ion exchange is presumed
3	HCO_3^- and Na^+ are dominant, normally indicates ion exchanged water, although the generation of CO_2 at depth can produce HCO_3^- where Na^+ is dominant under certain circumstances
4	SO_4^{2-} dominates, or anion discriminant and Ca^{2+} dominant, Ca^{2+} and SO_4^{2-} dominant, frequently indicates recharge water in lava and gypsiferous deposits, otherwise mixed water or water exhibiting simple dissolution may be indicated.
5	No dominant anion or cation, indicates water exhibiting simple dissolution or mixing.
6	SO_4^{2-}dominant or anion discriminate and Na^+ dominant; is a water type that is not frequently encountered and indicates probable mixing or uncommon dissolution influences.
7	Cl^- and Na dominant is frequently encountered unless cement pollution is present. Otherwise the water may result from reverse ion exchange of Na^+- Cl^- waters.
8	Cl^- dominant anion and Na^+ dominant cation, indicate that the ground waters be related to reverse ion exchange of Na^+- Cl^- waters.
9	$Cl^-$and Na^+ dominant frequently indicate end-point down gradient waters through dissolution

1.3.2. Comparison with the standards of drinking-water

The physicochemical results will compare with *WHO*'s drinking water standards and the Algerian standards, using Graphpad prism software, version 8, to determine which of our water samples are conform to the norms and which may have health risks.

1.3.3. Classification of samples by cluster dendrogram

The water samples were classified to unknown groups depends on its similarity of their physicochemical results using clusters dendrogram by Statistica software, version 8.

RESULTS AND DISCUSSION

2. RESULTS AND DISCUSSION

2.1. RESULTS:

2.1.1. Bacteriological quality

The bacteriological results showed that all samples are exempt from pathogenic bacteria:

- The Aerobic mesophilic germs were negative, no colonies grown up in TGEA medium.
- No colony detected in Cetrimide medium, which means *Ps. aeruginosa* was negative.
- No positive tubes with Lactose Broth, and BGLB media, so absence of Coliforms group.
- Anaerobic spores were also negative, no positive tubes with TSC agar.
- No positive tubes with ROTH D/C medium, absence of Enterococci.

2.1.2. Chemical contents

The physicochemical results of water samples are summarized in **tables 8** & **9**.

The pH of samples varied from 7 to 8, which is within the 6.5-8.5 range recommended for drinking water (see **tables 8** & **9**) (***Executive Decree*, 2014; WHO, 2017**).

The EC values vary from normal: *Lalla Khadidja*, *Texanna*, *El Goléa, Salsabil*, *Ain Bouglez*, *Righia* & *Besbassa*, into high in both mineral & spring water samples (131.9μc cm^{-1} – 1853.95 $\mu c/cm$) (see **tables 8** & **9**).

The EC value of more than 83% of water samples is higher than the allowable *WHO* value for drinking water: 400$\mu c/cm$. However, the EC threshold is 2800 $\mu c/cm$ in Algerian standards (***Executive Decree*, 2014**), which makes all water samples compliant with the Algerian permissible limit for EC.

The EC is proportional to the *TDS*. Drinking-water becomes significantly and increasingly unpalatable at *TDS* levels greater than about 1000*mg/L* (**WHO, 2017**): *Lavita*: 1569.43 *mg/L*, *Mouzaia*: 1494.33 *mg/L* and *Saida*: 1028 *mg/L*, also with the bottled spring water: *Soummam*: 1500 *mg/L* & *Arwa*: 1133.1 *mg/L*, whereas (45.23%) of samples exceeded the allowable limit of *TDS*: 600*mg/L* (see **table 8**).

Table 8: Physicochemical results of mineral water samples.

	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Salinity	Cl^{-}	SO_4^{2-}	HCO_3^{-}	NO_3^{-}	Dry residues 180°	Loss-on-ignition
Brands		µs/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
LallaKhadidja	7.8	282.31	242.46	24	14.9	03	0.7	116	35.45	30	122.03	2.30	41	6
Texanna	7.5	337.74	269.84	18	8	20	3.2	147.3	35.45	20.3	152.54	2.36	98	54
Guedila	7.5	819.5	654.75	54	35	30	2.4	356	70.91	108.09	305.1	4.67	400	90
Ifri	7.3	888.6	752.23	100	44	50	1.9	374	99.3	80	305.1	22.13	406	72
Alma	7.4	1135.64	961.4	130	57	18	5.5	481	141.81	100	335.6	23.5	602	243
Lavita	7.3	1853.95	1569.43	160	112	170	2.7	810	184.36	127.5	762.71	17.3	979	123
ElGoléa	7.8	326.21	280.2	16	11	33	14	142.3	35.45	44	91.53	9.83	192	146
Salsabil	7	256.53	220.32	24	3	25	4.2	120.8	71	6.7	76.3	10.23	155	135
Saida	7	1214.02	1028	66	56	69	2.8	530	127.63	120.5	274.6	38.2	501	27
Baniane	7.25	930.81	788	63	50	31.5	2.9	403	49.63	148	293	3.2	535	321
Mouzaia	7.3	1765.23	1494.33	100	100	155	3	763	156	200	714	18.5	705	91
Thevest	7.7	885.1	749.23	84	40	102.5	3.2	439	78	205.38	238	2.4	541	248
Toudja	7.6	432.6	346	41.7	12.33	27	1	231	63.82	16	171	0.93	262	120
Messerghine	8	713.93	570.41	22	15	73	1.2	342	132	79	213.6	5.54	368	305
Youkous	7.7	438.4	350.253	37	7	25	2.8	172.7	45	36	170	3.5	342	136
ManbaaElghezlane	7.44	955.5	809	115	19	80	1	385	120	160	270	22	719	202
WHO (1996, 2017)	6.5-8.5	400	Min 250 Max600	100	30	200	-	150	250	250	500	50	-	-
Algerian Standards (Ex.D 2014)	6.5-8.5	2800	-	200	-	200	12	-	500	400		50	1500	-

Table 9: Physicochemical results of spring water samples.

	pH	*EC*	*TDS*	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	*Salinity*	Cl^{-}	SO_4^{2-}	HCO_3^{-}	NO_3^{-}	*Dry residues 180°*	*Loss-on-ignition*
Brands		*µs/cm*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*
Ain-Bouglez	7.5	131.9	139.45	<15	2.1	10	1	55	42.54	18.3	30.5	8.49	36	2
Hassia	7.3	763.4	609.94	63	12	23	2.5	334	219.8	35.07	30.5	31.17	322	86
Tazliza	7.7	741.5	592.43	60	29	50	10.3	315	106.35	136	91.52	19.47	366	74
El Ghadir	7.6	941.2	796.8	69	17	45	2.9	406	63.82	148	366.1	35.11	510	136
Ouwis	7	992.1	839.85	63	30.5	51	1.3	435	78	176	274.6	12.30	534	125
Lajdar	7.8	712.54	569.3	60	35	40	2.9	310	42.54	62	305.1	8.42	359	59
Righia	7.6	132.85	140.5	<15	0	32	2	52.2	35.45	0	156.2	3.52	109	109
Fezguia	7.7	594.5	475	57	5	23	1.2	260	28.4	54	274.6	23.9	361	76
Mileza	7.44	1030	872	63	33	56	1.5	440	21.3	215	396.6	2.60	539	84
Nestle-Purelife	7.64	538.9	430.55	45	13	41.5	1.5	226	28.4	47	207.5	5.88	160	14
Togi	7.5	669.72	535.1	60	18.7	35	2.2	281	56.72	34	274.6	8.48	276	0
Ovitale	7.5	716.9	572.75	69	23	35.25	2.6	303	56.72	156	219.7	16.03	361	66
BirEssalam	7.4	872.9	738.91	69	22	41.25	2.1	371	28.4	111	341.7	3.38	501	33
Soummam	7.5	1772	1500	150	70	110	3.2	770	304.9	260	347.8	33.03	835	141
Arwa	7.2	1338.55	1133.1	125	43	66	1.3	579	163.1	237	329.5	60	581	79
MontDjurdjura	7.2	800.31	639.42	69	17.9	63	2.5	378	85.1	50	311.2	20.76	501	317
Ifren	7.4	441.8	353	42	5.9	26.25	2	226	28.36	30.4	201.35	2.60	116	1
Ayris	7.6	469.7	375.3	48	6.5	7	1	248	49.63	45	201.35	4.77	266	99
Star	7.35	739.2	590.6	105	13	20	1	399	78	49	286.8	31.36	543	201
Guerioune	7	547.34	437.31	54	2.5	14	1	261	142	60	135.6	17.76	404	305
Besbassa	7.7	345.34	275.92	69	1.7	45	1	135.4	60	12	70	11.27	279.9	120
SidiRached	7.55	608.21	485.94	80	5	50	2	241	60	35	207	35	526.5	141
El-Kantara	7.56	713.83	570.33	70	3	35	1.2	284	55	75	300	22	562	160
DjebelAmour	7.63	656.4	524.4	45	6	30	<0.2	262	45	100	240	43.85	307	120
Lajdar	7.8	712.54	569.3	60	35	40	2.9	310	42.54	62	305.1	8.42	359	59
Taya	7.5	473.5	378.3	50	11	65	1	187.1	117	99	65	28	490	200
Messad	7.6	769.2	614.6	75	7	60	1	307	170	160	120	1.19	600	322

The US Food and Drug Administration (*FDA*) describes natural mineral water as water containing at least 250 *mg/L* of *TDS* (**Ong et *al.*, 2009**), which is not carried out with two water samples labeled as natural mineral water: *Lalla khadidja*: 242.46 *mg/L* & *Salsabil*: 220.32 *mg/L*. The patability of water samples related to *TDS* concentrations is shown in **table 10**.

Table 10: The patability of water samples based on their *TDS* concentrations.

	TDS Concentrations (*mg/L*)				
Drinking water quality (WHO, 1996**)**	**Excellent** <300	**Good** 300-600	**Fair** 600-900	**Poor** 900-1200	**Unacceptable** > 1200
Mineral water samples	*Lalla khadidja Texanna El Goléa, Salsabil*	*Toudja Messerghine Youkous*	*Guedila Ifri, Baniane Thevest Manbaa el ghezlane*	*Alma Saida*	*Lavita Mouzaia*
Spring water samples	*Ain Bouglez, Righia Besbassa*	*Tazliza Lajdar Fezguia Nestle Pure life Togi Ovitale Ifren Ayris, Guerioune Sidi Rached El Kantara Djebel Amour Taya*	*Hassia El Ghadir Ouwis Mileza Bir-Essalam Mont Djurdjura Messad*	*Arwa*	*Soummam*

The Calcium concentrations exceed the WHO permissible limit (**WHO, 2017**) in six samples (they represent 14.28 %), where the upmost concentration is: 160 *mg/L*, for *Lavita* mineral water. In the spring waters: *Righia* & *Ain Bouglez* the calcium concentrations were below the detection limit (see **tables 8** & **9**).

The calcium concentrations of water samples were within the permissible limit of Algerian standards.

The magnesium concentrations ranged from 0 to 112 *mg/L*, (30.95 %) of samples exceeded the limit; the highest value detected with *Lavita* (see **table 8**).

The potassium and sodium concentrations of all samples are within the allowable range. Also, the chloride concentrations were within the WHO permissible limit unless with the spring water *Soummam*: 304.9 *mg/L* (see **table 9**), as well still conform to the Algerian standards, while (80.95 %) of samples exceeded the threshold limit of **NaCl** specified by the *WHO* at 150 *mg/L* (**WHO, 1996**).

According to *WHO* standards (**WHO, 2017**), the permissible limit for sulfate is 250 *mg/L*. We noticed that all water samples were within the threshold limit unless for the spring water *Soummam*: 260 *mg/L* however, it conforms according to the Algerian standards where the permissible limit for sulfate is 400 *mg/L* (see **table 8**).

The *WHO* threshold limit of bicarbonate is 500 *mg/L*, in all samples the bicarbonate values are within the standards, except for one mineral water: *Lavita*: 762.71 *mg/L* (see **table 8**).

The nitrate originates from organic matter degradation. Due to agricultural activities, it can reach groundwater and/or occasionally natural vegetation (**WHO 2017; Adamou et *al.*, 2020**), because it is very soluble (**Rodier et *al.*, 2009**)

The nitrate maximum limit is given by 50 *mg/L* according to *WHO* and *Algerian standards*. Only the spring water *Arwa* exceeded the permissible limit by 60 *mg/L* (**table 9**).

The loss on ignition measurement allowed us to determine approximately the organic matter in dry residues due to decompositions and volatilizations of mineral salts. Organic matter is the cause of such aesthetic concerns as color, taste & odor (**Rodier et *al.*, 2009**).

The highest organic matter concentrations were observed with: *Lavita*: 856 *mg/L* & *Soummam*: 694 *mg/L*, while the lowest concentration was with: *Righia* spring water: 0 *mg/L* (see **tables 8** & **9**).

Generally, we estimated a high organic matter in all water samples except for *Lalla Khadidja*, *El Goléa*, *Salsabil* & *Ain Bouglez*.

2.1.3. Hydrogeochemical facies

The chemical contents of water depend on the composition of rocks from which it is extracted and by geochemical processes (**Van der Aa, 2003**). The hydrogeochemical was evaluated by Piper trilinear diagram shown in **figure 15**, and Durov plot in **figure 16**.

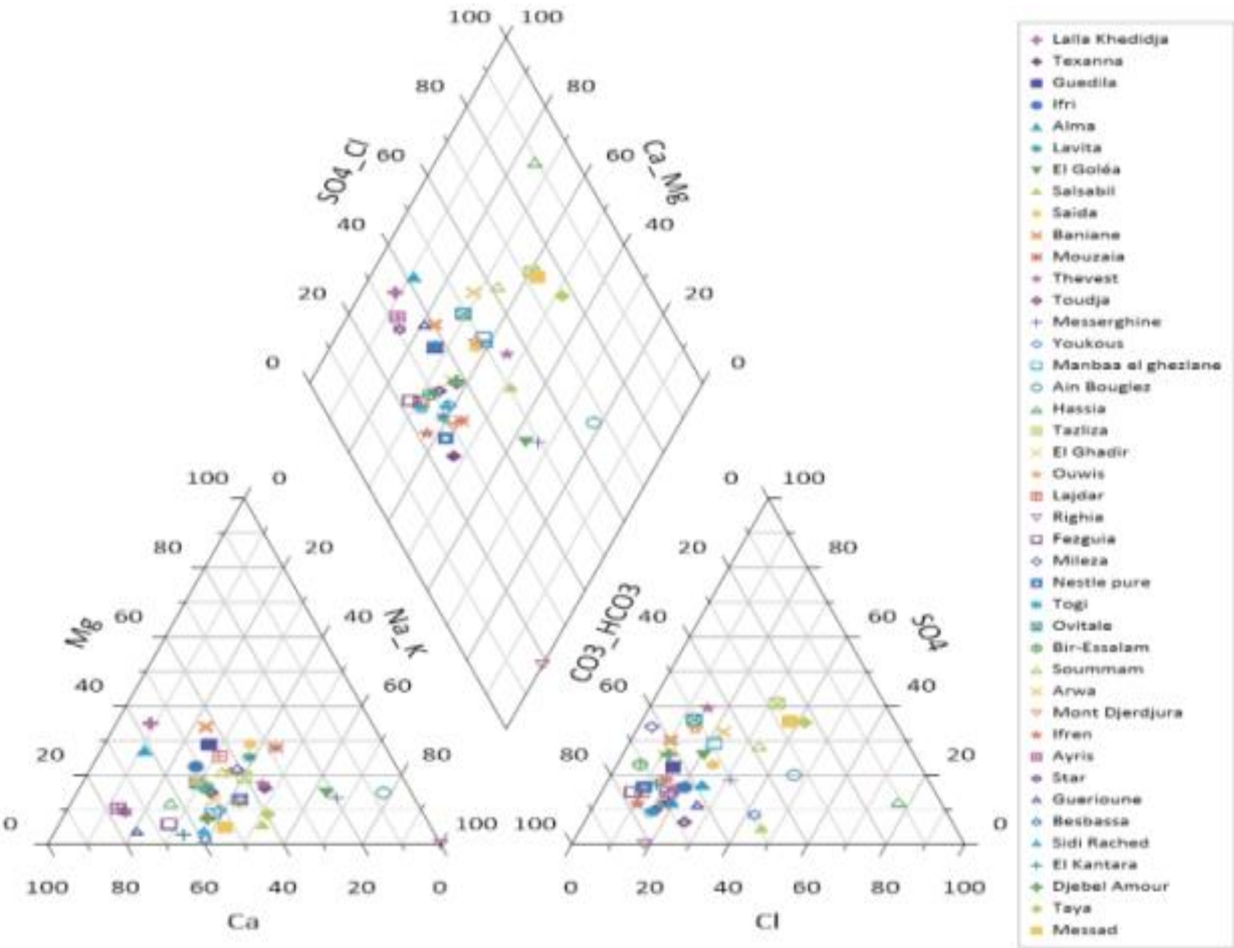


Figure 15: Piper Trilinear diagram showing the type of water samples.

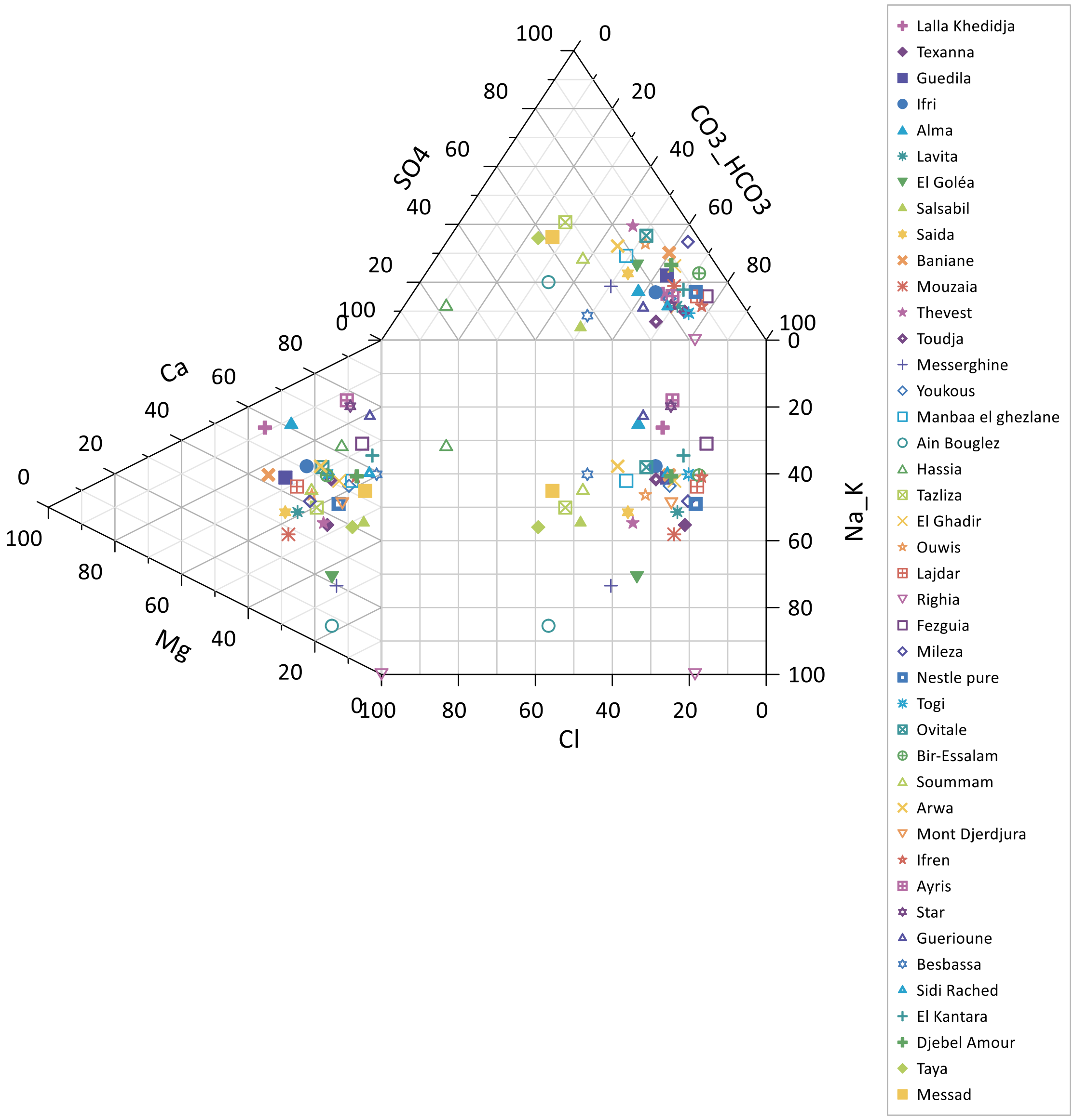


Figure 16: Durov plot showing the type of water samples.

The Piper diagram allowed us to classify the waters samples using the main cations $\boldsymbol{Ca^{2+}}$,$\boldsymbol{Mg^{2+}}$, $\boldsymbol{Na^{+}}$, $\boldsymbol{K^{+}}$ and, anions $\boldsymbol{Cl^{-}}$, $\boldsymbol{SO_4^{2-}}$, $\boldsymbol{HCO_3^{-}}$, $\boldsymbol{NO_3^{-}}$ (**Piper, 1944; Ravikumar et *al.*, 2015; Varol & Şekerci, 2018**).

Only (9.5%) of samples were classified as Normal earth alkaline waters: *Lalla Khadidja*, *Star*, and *Ayris* with dominant bicarbonate, *Alma* with dominant bicarbonate & chloride.

(14.28%) of samples belong to the alkaline water: *El Goléa*, *Messerghine*, *Salsabil* & *Ain Bouglez* with dominant bicarbonate, *Righia* with dominant chloride.

Most samples (76.19 %) were classified as Earth Alkaline water, where (80 %) of them belong to dominant HCO_3^-.

The data plotted on Durov diagram shown that more than 64.28% of water samples belong to field 6; SO_4^{2-}dominant or anion discriminate and Na^+ dominant; is a water type that is not frequently encountered and indicates probable mixing or uncommon dissolution influences.

(28.57%) of samples were belong to field 5; no dominant anion or cation, indicates water exhibiting simple dissolution or mixing.

(7.14%) belong to field 3; HCO_3^- and Na^+ are dominant, normally indicates ion exchanged water, although the generation of CO_2 at depth can produce HCO_3^- where Na^+ is dominant under certain circumstances.

2.2. DISCUSSION

The outcomes of bacteriological analyzes indicate that all samples were completely conforming to the Algerian drinking water standards (***Interministerial Decree*, 2016**) and the *WHO* standards.

The result of Piper and Durov diagrams was close to be similar, as they indicated that the majority of water samples belong to dominant bicarbonate and sulfate or discriminate anion (76.19% Earth alkaline water, and 64.28% field 6).

2.2.1. Comparison with the standards of drinking-water

We can observe clearly in **figures 17** & **18** Whether or not the samples comply or not with both Algerian standards and the WHO drinking water guidelines.

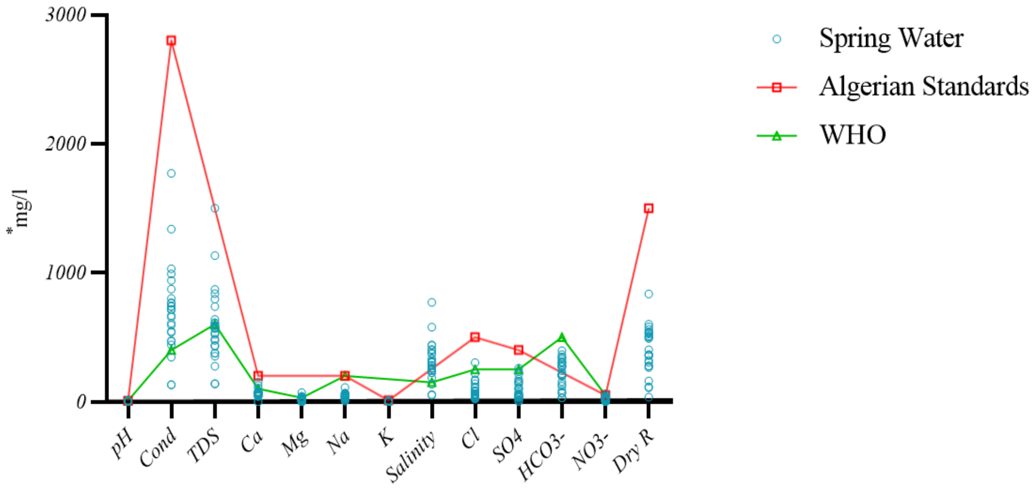


Figure 17: The chemical composition of spring water compared with *WHO* & Algerian standards.

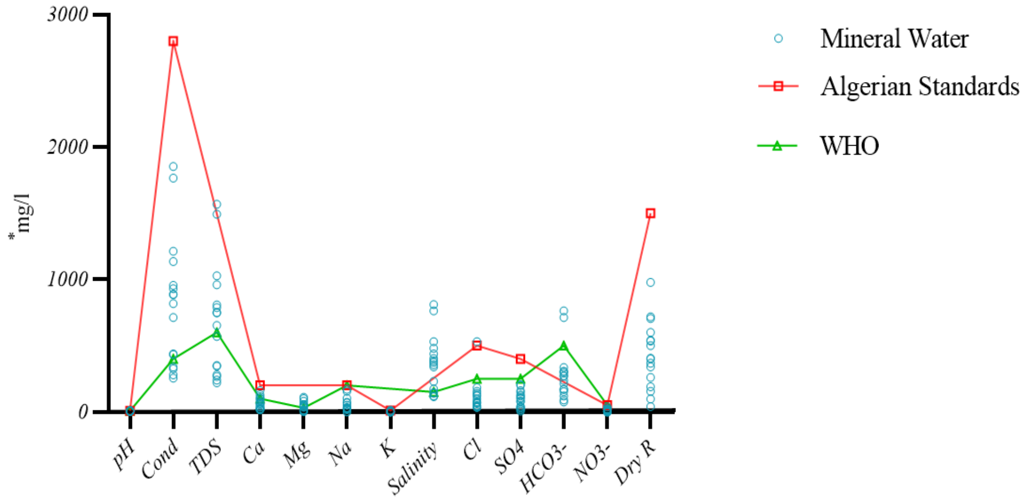


Figure 18: The chemical composition of mineral water compared with *WHO* & Algerian standards.

The Algerian standards' limits are very high which allows all the water types to be within the range even with their high mineralization, except for *Arwa* which has high nitrate level.

Conversely, the WHO drinking water standards are strict; allow only a few brands of bottled waters to be safely used as potable water.

Consequently, only 16.67 % were compliant with the norms: Ain *Bouglez, Righia* & *Besbassa* as spring water, *Texanna* & *El Goléa* as mineral water. *Salsabil* and *Lalla Khadidja* were compliant with the drinking water standards, but not as natural mineral water as indicated on their labels because their *TDS* concentrations were below the minimum level.

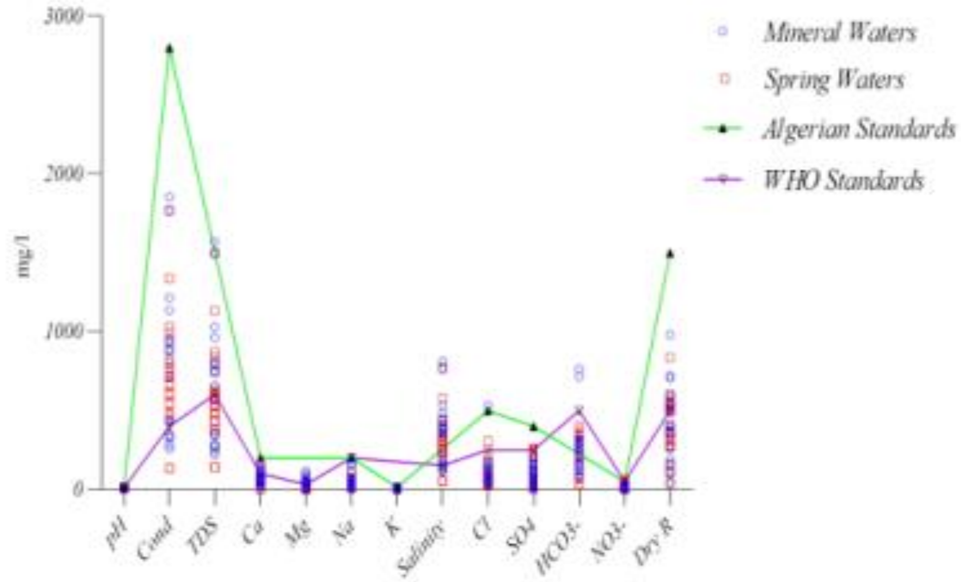


Figure 19: The chemical composition of water samples compared with *WHO* & Algerian standards.

As well **figure 19**, allowed us to notice the overlapping in the chemical parameters of spring and mineral water. No uniformity between the same-category brands.

We observed water brands labeled as natural mineral waters have low mineralization, per contra spring waters with very high mineralization, as *TDS* in *Soummam* is 1500 *mg/L*.

In this regard we readout that, the designation of bottled water as mineral or spring water was done randomly.

2.2.2. Classification of samples by cluster dendrogram

The comparison study is approved after classifying all samples into unknown groups depends on their similarity of their physicochemical results using clusters dendrogram (see **figure 20**).

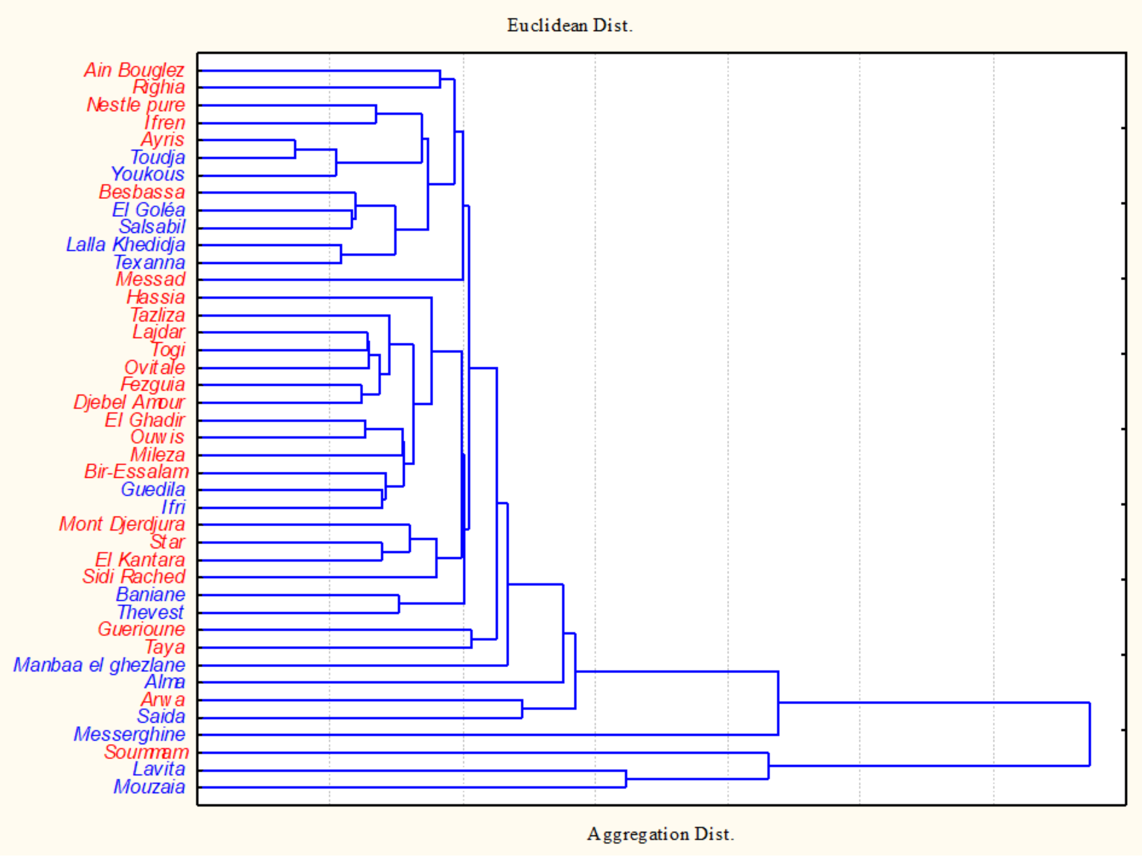


Figure 20: Dendrogram of 42 bottled water samples (mineral waters in blue color; spring waters in red color).

This classification is called Q-mode classification (**Belkhiri et *al.*, 2010**). *Ain Bouglez* was very close to *Righia*, had equally distant, which means they are similar; this is because both springs water filled from the same area.

From this point, we could count sixteen clusters with (70 %) of similarity, starting from the top of dendogram: **1** (*Ain Bouglez* & *Righia*) **2** (from *Nestle life pure* to *Texanna*) **3** (*Messad*) **4** (from *Hassia* to *Ifri*) **5** (From *Mont Djurdjura* to *Sidi Rached*) **6**

(*Baniane* & *Thevest*) **7** (*Gueriuone*) **8** (*Taya*) **9** (*Manbaa elghezlan*) **10** (*Alma*) **11** (*Arwa*) **12** (*Saida*) **13** (*Messerghine*) **14** (*Soummam*) **15** (*Lavita*) & **16** (*Mouzaia*).

We noticed that the mineral water: *Toudja*, *Youkous*, *El Goléa*, *Lalla Khadidja* are situated on the range close to spring water, which is consistent with **Hazzab** (**2011**) study's results, same remark with *Salsabil* & *Texanna*.

As well, some spring waters are situated close to the mineral waters range as *Arwa* & *Soummam*.

The chemical contents of bottled water as mentioned in their labels are presented below in **tables 11** & **12**.

Table 11: Chemical contents of bottled mineral waters as mentioned in their labels

							Concentration mg/l				
Parameters ***Water type***	***pH***	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	Cl^{-}	HCO_3^-	NO_3^-	NO_2	***Dry residues 180°***
Lalla khadidja	*7.22*	*53*	*7*	*5.5*	*0.54*	*7*	*11*	*160*	*0.42*	*00*	*187*
Texanna	*7*	*30*	*9.1*	*11*	*01*	*11*	*28.4*	*60*	*00*	*00*	*152*
Guedila	*7.35*	*78*	*37*	*29*	*2*	*95*	*40*	*/*	*4.5*	*<0.01*	*564*
Ifri	*7.2*	*99*	*24*	*15.8*	*2.1*	*68*	*72*	*265*	*15*	*<0.02*	*380*
Alma	*7*	*91*	*37*	*31*	*2*	*87*	*55*	*350*	*15*	*<0.01*	*628*
Lavita	*≤7.3*	*136*	*75*	*145*	*3*	*85*	*150*	*671*	*0.02*	2×10^{-5}	*1280*
ElGoléa	*7.4*	*24*	*7*	*28*	*4.6*	*36*	*20*	*/*	*2.4*	*trace*	*/*
Salsabil	*7.95*	*25*	*5*	*27*	*4*	*21*	*10*	*125*	*11.4*	*<0.01*	*199*
Saida	*7.5*	*68*	*50*	*58*	*02*	*65*		*/*	*15*		*478*
Baniane	*7.5*	*91*	*56*	*34*	*03*	*158*	*41*		*2.6*	*0.00*	*673*
Mouzaia	*6.5-7.3*	*136*	*75*	*145*	*03*	*85*	*150*	*671*	*0.02*	2.10^{-5}	*1280*
Thevest	*7.77*	*89.95*	*34.05*	*47.25*	*0.99*	*188*	*65*	*231.8*	*2.35*	*<0.01*	*588*
Toudja	*7.19*	*56.6*	*15.2*	*36*	*0.7*	*19.6*	*54.6*	*/*	*2.55*	*<0.01*	*256*
Messerghine	*7.2*	*52*	*42.0*	*45*	*3*	*50.0*	*78*	*260*	*5*	*0*	*320*
Youkous	*7.4*	*77.40*	*14.50*	*13.40*	*4.65*	*35.80*	*25.70*	*218.00*	*2.00*	*00.00*	*285*
Manbaa el ghezlane	*7.1*	*93*	*31*	*68*	*4*	*153*	*84*	*326*	*8.9*	*0.02*	*725*

Table 12: Chemical contents of bottled spring waters as mentioned in their labels

		Concentration mg/l									
Parameters Water type	**pH**	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	Cl^{-}	HCO_3^{-}	NO_3^{-}	NO_2	**Dry residues**
Ain Bouglez	6.87	4.6	3.75	29	1	10	30	/	9	0.06	140
Hassia	7.25	63	8	20	1.0	7.0	36	198	9.2	00	291
Tazliza	7.32	48	20	48	8	96	76	104	19.97	0.01	407
El Ghadir	7.5	111	28	25	3	106	37	317	25	00	700
Ouwis	7.42	106	25	60	2	177	48.59	261	18.30	<0.01	724
Lajdar	7.53	64	37	30	4	66	41	308	<50	<0.1	660
Righia	6.70	08	03	12.8	0.35	01	19.3	24.40	2.5	0.02	100
Fezguia	7.22	78.15	35.23	22	4.1	33.25	35.5	285	0.73	0	415
Mileza	7.33	111	34	29	1	190	10	311	3.2	<0.01	680
Nestle Pure life	7.8	55	17	>12	0.5	33	>15	210	4.6	0	372
Togi	7.46	73.41	19.25	36	1.8	28.90	43.76	/	5.93	<0.01	366
Ovitale	6.92	91	14	30	1	86	50	214	<15	0	420
Bir-Essalam	7.44	62.88	13.47	22.8	2.1	71.5	23.1	/	<15	<0.02	285
Soummam	7.21	114	32	71	2	196	78	293	19.2	<0.01	755
arwa	7.33	120	23	56	1	104	100	256	46.5	<0.01	450
Mont Djurdjura	7.67	103	28	54	01	56	97	357	30	<0.01	700
Ifren	7.48	68.8	10.69	32	2.4	62.5	17.04	283.04	3.22	<0.01>	300
Ayris	7.78	65.6	6.8	28.5	1.9	75	37	234.24	2.7	0.01	276
Star	7	115	33	30	1.8	95	82	330	37.2	< 0.02	490
Guerioune	6.98	55.8	26.52	14	1	100.00	50	134.2	12	/	376
Besbassa	7.29	54.16	2.64	5	2	4.00	10	164.70	9.00	<0.01	206
Sidi Rached	7.39	134.38	6.69	29.21	2.45	139	50	235	21.80	0.00	610
El Kantara	7.32	90	37	36	3	162	59	247	9.60	<0.01	636
Djebel Amour	7.13	81	14	21	0.2	64	38.4	198	29.26	<0.01	410
Taya	7.3	47.25	12.48	55	1	82	110	/	17.37	0.01	400
Messad	7.13	79	27	50	02	156	275	40	2.3	<0.01	611

As the tables (11 & 12) shown, we could see clearly that the chemical compositions we found in laboratory of the majority of brands are totally different from what it mentioned in their labels.

It is given that the natural mineral water characterized by the constancy of its composition and the stability of its discharge through a long period of time (**Codex 108-1981**). So we can say that the labels are falsified, where the composition put randomly, or they have not been updating since the first bottling process.

CONCLUSION

CONCLUSION

PhD thesis cannot be expected that it will cover all the aspect of an area of knowledge, the study area has been limited to assess the quality of the most bottled water purchased in Algeria; bacteriological control, chemical control of the major elements then compared our results by the standards.

Forty-two water brands were analyzed; which represent more than 95% from the brand waters bottled in Algeria, taking in consideration; the granting, the exploitation licenses given by the authorities, and their expiration.

All samples were bacteriologically safe as the results shown, which is conform to the standards says that underground waters are free from pathogenic bacteria, and the purity of mineral waters.

The hydrochemical quality with Piper diagram showed that 76.19% of samples are Earth Alkaline water with bicarbonate dominants mostly. And with Durov diagram showed that 64.28% of the samples are sulfate dominant or anion discriminate and sodium.

The physicochemical data of 14 parameters compared with world health organization and the Algerian standards. 83.33 % of brands did not conform to the *WHO*'s drinking water guidelines, which may pose risk to consumers with health issues, infants, young children, debilitated people, & the elderly.

Furthermore, (97.619%) of the brands are conform comparing with Algerian standards, which allow all the brands to be safe for consumption except with the spring water Arwa which represent a high nitrate concentration (60mg/L).

The large differences between the local and the international standards may affect the export trade of bottled water and mainly consumer's health.

This contradiction in norms appeared also in other countries, where **Ganau (2012**) found out that the limit recommended by the WHO is in some cases lower than the legal limit in Catalonia.

We concluded that not all bottled water are safe for all categories of people, the selection between water types must be based on chemical composition mentioned in labels and the health condition of consumers. For example; Patients with calcium deficiency or osteoporosis must choose water with high mineralization; rich by calcium. But a person in normal health condition should choose water conform to the guidelines of drinking-water to be safe.

That’s why we suggest adding some important information on label, such as *TDS* concentration.

We recommend that the Algerian standards adapt to international drinking-water standards and apply strict control of the bottled water labels and their updating, whenever required to avoid the falsification and random nomination among spring and mineral water.

The challenge facing the qualitative and quantitative determinations of inorganic and organic compounds present in bottled water is difficult mainly because of:

- The low levels of individual compounds present in samples.
- The complex composition (high degree of mineralization).
- Interactions between the constituents present in samples, possible changes in composition during transport and storage as a result of reactions and the potential desorption of constituents from packaging materials.
- The interdependence between constituents present in samples for example the Ca; Mg ion ration.

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APPENDICES

Appendix 1: Properties of water (Ordinary water with natural isotopic composition & atmospheric pressure (1 atm = 101 325 Pa) (**Gordalla et *al.*, 2007**).

Property	**Value**
Molar mass M	18.012 g/mol
Standard enthalpy of formation $\Delta_f H^0$	-286.2 kJ/mol
Standard entropy of formation $\Delta_f S^0$	69.98 J/(mol×K)
Melting point θm	0°C
Boiling point θ_b 100 °C Triple point	θb 100 °C θ_t= 0.01 °C, p_t= 6.133×10^2 Pa
Critical point	θ_c= 373.98 °C, p_c=22.05□10^6 Pa p_c= 322 kg/m
Density ρ liquid water Ice I	 997.05 kg/m^3 (25 °C) 999.87 kg/m^3 (0 °C) 916.8 kg/m^3 (0 °C)
Thermal expansion coefficient α	257.1×10^{-6}/K (25 °C)
Isothermal compressibility χ_T	4.525×10^{-4}/Pa (25 °C)
Specific heat capacity c_p liquid water **1.1.** Ice	 4.180 kJ/(kg×K) (25 °C) 4.191 kJ/(kg×K) (10 °C) 4.228 kJ/(kg×K) (0 °C) 2.072 kJ/(kg×K) (0 °C)
Vapour pressure p	3176.2 Pa (25 °C) 1228 Pa (10 °C) 611 Pa (0 °C)
Latent heat of vaporisation Δ_{vap} h	2243.7 kJ/kg (25 °C) 2256.6 kJ/kg (100 °C)
Latent heat of fusion Δ_{fus} h	333.69 kJ/kg (0 °C)
Cryoscopic constant K_f	1.853 K×kg/mol
Ebullioscopic constant K_b	0.515 K×kg/mol
Surface tension σ	7.423×10^{-2} N/m (10 °C) 7.20 ×10^{-2} N/m (25 °C) 5.891×10^{-2} N/m (100 °C)

Dynamic viscosity **η**	0.8903×10^{-3} Pa×s (25 °C) 1.307×10^{-3} Pa×s (10 °C)
Refractive index n	1.3325 für **λ** = 589 nm (25 °C)
Dielectric constant **ε**	78.46 (25 °C) 87.81 (0 °C)
Sound velocity c_{sound} in distilled water in sea water	 1496.7 m/s 1531 m/s
Thermal conductivity **λ** liquid water ice	 0.602 W/(K×m) (20 °C) 0.565 W/(K×m) (0 °C) 2.25 W/(K×m) (0 °C)
Ion product K_W	1.008×10^{-14} (pK_w=14.00) (25 °C) 0.292×10^{-14} (pK_w=14.53) (10 °C) 0.184×10^{-14} (pK_w=14.73) (5 °C) 0.114×10^{-14} (pK_w=14.94) (0 °C)

Appendix 2: Natural mineral water in its packaged state shall contain no more than the following amounts of the substances: (**Executive Decree, 2014**)

- Antimony 0.005 mg/L
- Arsenic 0.01 mg/L
- Barium 0.7 mg/L
- Borate 5 mg/L
- Cadmium 0.003 mg/L
- Chromium 0.05 mg/L
- Copper 1 mg/L
- Cyanide 0.07 mg/L
- Lead 0.01 mg/L
- Manganese 0.4 mg/L
- Mercury 0.001 mg/L
- Nickel 0.02 mg/L
- Nitrate 50 mg/L
- Nitrite 0.1 mg/L
- Selenium 0.01 mg/L.

Appendix 3: Measurement uncertainty of our physicochemical results (only Type A uncertainty was taken into consideration)

Parameter	**Expanded uncertainty µ**
pH	±0.109
EC	±1.410 µs/cm
TDS	±1.269 mg/L
Calcium	±0.067 mg/L
Magnesium	±0.080 mg/L
Sodium	±0.109 mg/L
Potassium	±0.052 mg/L
Salinity	±0.674 mg/L
Chloride	±0.259 mg/L
Sulphate	±0.853 mg/L
Bicarbonate	±0.905 mg/L
Nitrate	±0.044 mg/L
Dry residues 180C	±0.674 mg/L
Loss-on-ignition	±1.044 mg/L

*Student factor = 2.132 for a level of confidence 95%.

ABSTRACTS

ABSTRACT

Forty-two different brands between mineral & spring waters were purchased from varied markets in Algeria.They have been analyzed for their bacteriological quality and chemical major elements. The results showed that all the brands presented good bacteriological quality (Absence of *E. coli*, Total coliforms, *Ps. aerugenosa, enterococci* & anaerobic spores). Piper diagram shown that (76.19%) of the samples were classified as Earth Alkaline water, where (80%) of them belong to dominant HCO_3^-.Durov plot shown that (64.28%) belong to anions dominant type By comparing the results with the WHO standards we found that only (16.67%) of the brands are compliant with the standards: *Ain Bouglez*, *Righia*, & *Besbassa* as spring waters, *Texanna*, *El Goléa*, *Salsabil* & *Lalla Khadidja* as mineral waters, those last two they have not enough *TDS* to consider them as mineral waters like mentioned in their labels, which confirmed by dendrogram classification. Otherwise, when the results compare with the Algerian standards, all the brand waters turned to be compliant with them except for *Arwa*. Consumers must be very wary about the consumption of bottled water, especially if they already have health issues because they cannot make a choice only from the labels which are mostly different from the real chemical composition.

Keywords: Algeria, health-related effects, mineral water, Piper diagram, Durov diagram, spring water.

RÉSUMÉ

Quarante-deux marques différentes entre eaux minérales et eaux de source ont été achetées sur des marchés variés en Algérie, elles ont été analysées pour leur qualité bactériologique et leurs éléments chimiques majeurs. Les résultats ont montré que toutes les marques présentaient une bonne qualité bactériologique (Absence d'*E. coli*, Coliformes totaux, *Ps. aerugenosa*, entérocoques et les spores anaérobies). Le diagramme de Piper a montré que (76,19 %) des échantillons étaient classés comme eau alcaline terrestre, où (80 %) d'entre eux appartiennent à des HCO_3^- dominantes. Durov plot a montré que (64,28%) des échantillons appartiennent au type des anions dominant. En comparant les résultats avec les normes de l'OMS, nous avons constaté que seulement (16,67%) des marques sont conformes aux normes : *Ain Bouglez, Righia, et Besbassa* comme eaux de source, *Texanna, El Goléa, Salsabil et Lalla Khadidja* comme des eaux minérales, ces deux derniers ils n'ont pas assez de TDS pour les considérer comme des eaux minérales comme mentionné dans leurs étiquettes, ce qui a confirmé par la classification dendrogramme. Autrement, lorsque les résultats sont comparés aux normes algériennes, toutes les marques d'eaux se sont avérées être conformes à celles-ci à l'exception d'*Arwa*. Les consommateurs doivent être très prudents lorsqu'ils consomment de l'eau en bouteille, surtout s'ils ont déjà des problèmes de santé car ils ne peuvent pas choisir en fonction de l'étiquette, qui souvent ne reflète pas la véritable composition chimique.

Mots clés : Algérie, effets sur la santé, eau minérale, diagramme de Piper, diagramme Durov, eau de source.

الملخص

اثنان و اربعون علامة ما بين مياه معدنية و مياه منبع تم اقتناؤها من مختلف المحلات في الجزائر، تم تحليل جودتهم البكتيريولوجية و العناصر الكيميائية الغالبة. اظهرت النتائج ان جميع العلامات التجارية ذات جودة بكتيريولوجية جيدة (غياب الايشيريشيا القولونية، المكورات الكلية، بسودوموناس ايروجينوزا الفصيلة الزنجارية، المكورات المعوية و العقد الاهوائية). يوضح مخطط بيبر أن (76.19%) من العيينات صنفت على انها مياه ارضية قلوية، حيث (80%) منها تنتمي للبيكاربونات السائدة.كما يظهر مخطط دوروف ان 64.28% من المياه تحتوي ايونات سائدة. بمقارنة النتائج مع معايير منظمة الصحة العالمية وجدنا ان (16.67%) فقط من العلامات متوافقة مع المعايير: عين بوقلاز، ريغيا و بسباسة كمياه منبع. تكسانة، القولية، سلسبيل و لالة خديجة كمياه معدنية، هذين الاخيرين ليس فيهم من الاملاح المذابة الكلية ما يكفي لتصنيفها كمياه معدنية كما يظهرها الوسم، و هذا ما اكده تصنيف الدوندروغرام. خلافا لذلك، عند مقارنة النتائج بالمعايير الجزائرية ، نجد ان جميع العلامات التجارية للمياه اصبحت مطابقة للمعايير باستثناء: مروى. يجب ان يكون المستهلكون حذرين للغاية بشان استهلاك المياه المعبأة، خاصة اذا كانت لديهم بالفعل مشاكل صحية لأنه لا يمكنهم الاختيار اعتمادا على الوسم الذي في الغالب لا يعبر عن التركيب الكيميائي الحقيقي.

الكلمات المفتاحية

الجزائر، التأثيرات المتعلقة بالصحة، المياه المعدنية، مخطط بيبر ،مخطط دوروف، مياه الينابيع.