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Chemical Composition of Selected Brands of Bottled Water Commercilaized in Tripoli, Libya †

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Abstract: Bottled water is one of the sources of drinking water in many developed and developing countries, including Libya. One of the greatest concerns is the health effects of low mineral content or lack of essential minerals in bottled water. The aim of this study was to evaluate the chemical quality of selected brands of bottled water in Tripoli. Water quality parameters such as physical (color, turbidity, total dissolved solids (TDS)), chemical (pH, total hardness (T.H), sodium (Na^+), potassium (K^+), magnesium ($Mg_2{}^+$), calcium (Ca^{2+}), chloride (Cl^-), bicarbonate ($HCO_3{}^-$), carbonate ($CO_3{}^{2-}$), sulphate ($SO_4{}^{2-}$), and nitrite ($NO_2{}^-$), were determined using standard procedures. The results showed a widespread in the characteristics of investigated bottled waters, yet the majority met the various national and international bottled water standards for physic-chemical parameters except for pH (5 brands (<6.5)).

Keywords: bottled water; drinking water quality; libyan standards for bottled water; WHO standards for drinking water

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1. Introduction

One of the main problems faced by the inhabitants of Tripoli is the lack of drinking water. The artificial river project is the main source of water supply for the city, but at the same time it is considered an unstable source due to frequent interruptions due to the political conflicts that have taken place in the region since 2011. On the other hand, the residents of Tripoli do not feel completely comfortable with the water coming from the man-made river and therefore, do not consume it for drinking but in other uses such as agricultural and sometimes industrial uses. This discomfort has been resulted due to several reasons, most notably the lack of quality of this water and perhaps their feeling that the official authorities do not carry out the necessary sterilization and treatment before the distribution of water to citizens through distribution networks [1].

As a result of the ongoing water shortage, residents of Tripoli and other Libyan cities have resorted to other solutions to obtain safe drinking water, including bottled water. Residents choose bottled water over tap water because it is perceived to be safer and higher quality than tap water. Bottled water sold in Tripoli comes in different capacities and packages ranging from 200 mL to 20 L. Small containers (200 mL–500 mL) are the most consumed by the population due to their easy handling and transportation. For this reason, bottled water has been well accepted for consumption in homes, workplaces, and many service facilities such as hospitals, schools, universities, and other places [2]. It has been noted that, in Libya, it is allowed (it does not necessary mean it is legally) to have 18 L water bottles (containers) which may increase the probability of contamination because bottles will stay opened for an extended time [3–5].

In Tripoli (Figure 1), the majority of households indicated relying on bottled water as their main source of water (61.2%) due to instability in the main public water supply network following recent maintenance work [6]. The water supply network could be cut for long periods of time when armed groups controlled it in struggle for influence over an area in the city [7,8]. The purchase of bottled water as an alternative drinking water source implies an additional financial burden for the residents in Tripoli.

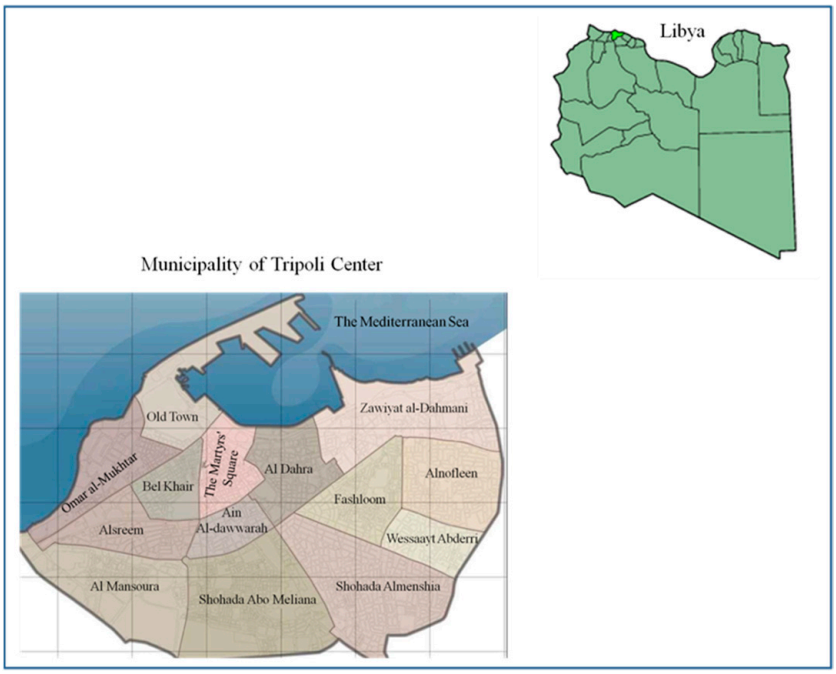


Figure 1. Map of Libya showing the location of the municipality of Tripoli Center.

Despite the lack of local scientific studies on the quality of bottled water produced and sold in Tripoli, and the high cost of bottled water, in recent years Tripoli has witnessed an increase in the number of factories producing this water. Furthermore, bottled water was widely accepted among people from different segments of society [9,10].

The production of bottled water in Libya began in 1959 with the establishment of the Bin Gheshir water plant. In 2004, there were about 43 local factories and the production of these factories reached 109,586 L of water. Recently, many water treatment and bottling plants have been deployed in Libya in general and in Tripoli in particular. The products of these plants are becoming widely available in the Libyan shops and markets today. The main source of bottled water sold in Tripoli is pumped from drilled wells via reverse osmosis desalination process [11].

The increasing demand for bottled water has coincided with a lack of awareness regarding the health effects that may result from prolonged and continuous consumption [12]. The World Health Organization (WHO) provides general guidelines for drinking water quality [13]. In Libya, the Libyan National Center for Standardization and Metrology (LNCSM) formulates national standards for drinking water and other fields of interest. The Libyan Standards (LS) 82 (1992) provides specifications of drinking water while, the Libyan Standards (LS) 10 (1997) and (LS) 10 (2008) provide specification of bottled drinking waters [14,15].

Studies elsewhere have shown non-compliance and irregularities in the analytical and chemical composition of the bottled drinking water. Furthermore, studies have shown contamination and dubious labeling of bottled drinking water [16]. Bottle labeling of the chemical composition is of great concern and, for example, cases of undervaluing and exaggeration have been reported [17]. On the other hand, the contamination of bottled water may result in different stages of the production process, including packaging, distri-

bution, maintenance and unsuitable storage conditions. Therefore, compliance with the sanitary regulations during production and packaging is of great importance. Additionally, choice of appropriate equipment, maintenance of equipment and control of the packaging operations shall ensure no damage of the product occurs or will occur during its life. The label shall comply with the regulation and give clear instructions to consumers for storage, preparation and use of the product where necessary [12].

Despite the increase consumption of packaged water in different sizes in Tripoli, there are not readily available studies in literature, there are either scanty or no published reports in literature concerning chemical composition of the bottled drinking water sold in Tripoli. Therefore, the aim of this study is to investigate the chemical composition of 17 brands of bottled water sold in Tripoli and its suburbs. The study primarily focused on the physic-chemical water quality, their compliance with national and international drinking water standards and potential health implications associated with consumption of the bottled drinking water. In addition, the physic-chemical water quality content is to be compared with labels shown by manufacturers (Table 1). The results were then compared with threshold limit values established by Libyan and international regulatory organizations to ascertain their suitability for human consumption as drinking water (Table 2).

Table 1. Chemical and Physical analysis of bottled waters in comparison of the constituents reported on their labels.

Brand	pH		Total Hardness		Sodium		Potassium		Magnesium		Calcium		Chloride		Bicarbonate		Carbonate		Sulphate		Nitrite		TDS	
	M	L	M	L	M	L	M	L	M	L	M	L	M	L	M	L	M	L	M	L	M	L	M	L
T1	6.0	6.7	5	2	6	4.06	0	0.7	5	0.5	0	0.8	8	7.09	10	6.1	5	-	4	-	0	-	13	42
T2	6.4	7.2	15	40	16	4.4	18	-	100	-	1	-	20	-	400	34.16	200	-	2	4.7	0	-	66	>50<
T3	6.4	7.2	5	-	9	1.1	0.9	-	14	2.3	0	8.1	5.2	0.84	15	29.3	10	-	2	-	0.03	-	37	-
T4	6.2	7.2	15	45	32	15	5.4	2	24	-	2	-	48	-	25	16	15	-	0	-	0	-	74.7	-
T5	6	-	5	-	6	6.0	0	0.6	5	2.4	0	4.6	7.8	9.93	10	12.2	5	-	4	4.4	0	-	13	30
T6	7.2	6.74	-	8.42	-	13	-	1	-	1.3	-	1.2	23.5	23	50	16	25	-	8	6	0.04	-	78	<100
T7	7.3	7.0	40	-	28	52.9	6.8	0.2	50	1.8	3	1	40	14.7	40	18.3	20	-	4	9.6	0.03	-	100	<200
T8	7.34	7.2	0	-	16	80	0.8	0.2	14	5.28	3	24	24.5	34	30	19.52	15	-	2	24	0	19.8	116	144.3
T9	7.8	-	20	-	20	-	2.2	-	3.40	-	-	-	30	-	20	-	10	-	3	-	0	-	57.2	-
T10	7.7	6.7	20	–	7.5	16	2.4	2	5	4	0	7	10	34	70	26	35	-	0	15	0	-	33.8	60.12
T11	8.1	7.39	0	<15	8.5	2.06	0	<0.5	13	0.5	1	5.3	11.5	0.98	95	14.2	45	-	0	2.03	0	-	44.85	20
T12	7.5	-	30	-	22	-	0.1	-	7	-	0	-	32.5	-	60	-	30	-	3	-	1.65	-	122.8	-
T13	7.3	-	10	-	9	-	2.1	-	7	-	2	-	13	-	65	-	30	-	10	-	0	-	88.4	-
T14	7.1	7.0	-	2.8	-	3.8	-	2	-	4.8	-	8	-	21.2	-	4	-	-	-	3.3	-	-	95.55	≤80
T15	7.3	7.2	60	-	12	-	2.3	-	30	-	1	-	19	-	55	-	30	-	2	-	0	-	68.9	<150
T16	6.9	7.0	10	-	8	5	0.4	0	30	0.12	0	0.2	0.1	8.1	25	20.1	10	-	1	0	0	-	59.8	50
T17	7.0	7.0	25	-	32	8.8	2.8	0.5	21	8.5	13	8	48	31	35	30.8	15	-	2	7.8	0.03	-	114	<100

M = Measured L = Labeled.

Table 2. Present regulations and standards for the bottled drinking water.

Chemical Element	Proposed Libyan Standards (2016)	Mexican Standard Limits NOM-0127-SSA1-1994	Norma USA: 40 CFR Part 141 [4]	Colombian Standard: 2115 of 2007
Arsenic (As)	0.01	0.05	0.01	0.01
Barium (Ba^{2+})	0.7	0.7	2	0.7
Beryllium (Be)	0.001	-	0.001	-
Cadmium (Cd^{2+})	0.003	0.005	0.005	0.003
Calcium (Ca^{2+})	-	-	-	60
Chloride (Cl^{-})	250	250	-	250
Chromium (Cr)	0.05	0.05	0.1	-

Table 2. *Cont.*

Chemical Element	Proposed Libyan Standards (2016)	Mexican Standard Limits NOM-0127-SSA1-1994	Norma USA: 40 CFR Part 141 [4]	Colombian Standard: 2115 of 2007
Copper (Cu)	1.0	2	1.3	1
Fluoride (F^-)	1.5	1.5	-	-
Iron (Fe)	0.3	0.3	0.3	0.3
Lead (Pb)	0.005	0.01	0.015	0.01
Magnesium (Mg^{2+})	75	-	-	36
Manganese (Mn^{2+})	0.05	0.15	-	1
Mercury (Hg)	0.01	0.001	0.002	-
Nitrate (NO_3^-)	45	10	10	-
Nitrite (NO_2^-)	3	1	1	-
Potassium (K^+)	12	-	-	-
Sodium (Na^+)	200	200	200	-
Sulfate (SO_4^{2-})	250	400	-	250
TDS	100–500	1000	-	-
Turbidity NTU	5	5	-	2
Total hardness (TH)	200	-	-	-
pH	6.5–8.5	6.5–8	-	-

2. Materials and Methods

2.1. Sampling

During the summer months of July, August and September 2019, 17 brands of bottled waters available on the Libyan market were purchased in randomly selected shops in the Capital Tripoli and its suburbs. To keep the brand names anonymous, the samples were given code names and this convention is used throughout the study.

The selected bottled waters did not contain added gas and were purchased in the 0.2 L (T3, T7 and T8) and 0.5 L (T1, T2, T4, T5, T6, T9, T10, T11, T12, T13, T14, T15, T16 and T17) sizes. All the analyzed waters were contained in plastic bottles made of polyethylene terephthalate (PET) with a polyethylene (PE) cap. Selected bottled waters were inspected and verified to be in good condition with the caps and protective seal intact before purchase. All samples were purified (desalinated) water and were considered the most consumed and best-selling brands among the other bottled waters in Tripoli. In addition, the bottled water samples obtained were from the same 2019 production year.

All bottled waters were analyzed at the water quality laboratory of the environmental rectification department of Tripoli Center Municipality. One liter of water per brand was considered. Each water sample was analyzed for 9 chemical elements and ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-} and NO_2^-).

2.2. Chemical Analysis

Physic-chemical analysis was performed in accordance with standard methods. pH was determined using pH meter (Adwa AD1000, Adwa Instruments, Szeged, Hungary), Total dissolved solids (TDS), conductivity were measured using TDS/conductivity meter (Lovibond ® SensoDirect Con 110, Lovibond, Dortmund, Germany), The measurement of sodium and potassium and other cations and anions was accomplished by photometer

multiparameter (Palintest-Model 7100-Portable, Palintest, Beijing, China). The turbidity level was measured by the Hach turbidity meter device (USA).

2.3. Statistical Analysis

A statistical analysis was performed on the data measured for each brand of bottled water; the calculation of the mean, the standard deviation and the confidence interval for each parameter are highlighted. The results obtained were subjected to statistical analysis for analysis of variance using SPSS 15.0.

3. Results and Discussion

In this study the amount of pH, TDS and ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-} and NO_2^-) was surveyed, in 17 samples of bottled waters in Tripoli, Libya. The results showed that there were differences between amounts of these ions in their water contents and label insertion on the bottles. The standard deviation, mean, and maximum and minimum values were obtained and presented in Tables 3 and 4.

Table 3. Statistical variables of the analyzed samples.

Brand	pH	Total Hardness	Sodium	Potassium	Magnesium	Calcium
Average	7.031	17.333	15.466	2.946	21.893	1.857
Standard dev	0.612	15.797	8.982	4.464	24.321	3.270
Sup interval	7.322	24.842	19.736	5.068	33.454	3.411
Lower interval	6.740	9.823	11.196	0.824	10.331	0.302

Table 4. Statistical variables of the analyzed samples.

Brand	Chloride	Bicarbonate	Carbonate	Sulphate	Nitrite	TDS
Average	21.318	62.812	31.258	2.937	0.106	69.58
Standard dev	14.489	90.120	44.982	2.656	0.398	33.10
Sup interval	28.206	105.653	52.633	4.200	0.295	85.32
Lower interval	14.430	19.971	9.866	1.674	−0.083	53.85

The hydrogen ion concentration (pH) values of the real contents are slightly different from the label contents. The measured pH values have a range of 6.0 to 8.1 which is within the Libyan Standards of drinking water (LNS 10:2016). Although, no health-based guideline value is projected for pH due to its insignificant health concerns in drinking water [16], continued consumption of water with low pH may pose a health hazard to consumers by damaging certain body tissues. Furthermore, low pH has implication on the solubility and thus the bioavailability of other substances especially the heavy metals which are harmful to humans [17,18].

Measured total hardness (TH) in all samples were below 60 mg/L which is within the permissible (TH) levels of the Libyan standards. However, it was also observed that around 65% of the samples violated the Libyan standards in not writing the total hardness on their labels (Table 1). The remaining samples showed significant difference between measured and labeled values, being the labeled values the greatest.

The concentration ranges for selected major ions in bottled water were (mg/L): 0–13 for calcium; 0–18 for potassium; 5–100 for magnesium and 6–32 for sodium. The overall mean for the selected major ions (calcium, potassium, magnesium and sodium) for bottled water is very different from the labeled values. Table 4 illustrates the results for the measured and labeled parameters and guideline values recommended by WHO [19] and the proposed Libyan standards (2016).

All the samples tested were below the suggested guidelines but a closer examination of major ion composition data for the samples (Table 5) reveals that concentrations for most of the major ions are considerably below the applicable standards. TDS values indicate

the deficiency of minerals in the Libyan bottled water. Previous studies have shown that long term consumption of water low in minerals such as calcium and magnesium do in fact pose a number of health risks. Both calcium and magnesium play important roles in the human dietary needs [20]. Calcium and magnesium are vital nutrients in the human body [21]. In addition to having beneficial effects on the human bone structure, calcium and magnesium are linked to the reduced frequency of heart diseases and osteoporosis, respectively [22]. Consuming water with low concentrations of minerals such as calcium and magnesium are also harmful for the body because water low in mineral content could lead to depletion of one's supply of essential nutrients [23]. Additionally, low-mineral water acts as osmoreceptors causing a net flow of minerals from erythrocytes (red blood cells) into the plasma and between intracellular and interstitial fluids. This further confirms the loss of minerals from one's body due to the consumption of low mineral water. Therefore, if consumers were to rely on the mineral-deficient brands of water for long periods of time, essential minerals such as calcium, potassium, magnesium and sodium will leach out from the body [24].

Table 5. The comparison of hydro chemical parameters of the selected brands of bottled water with WHO (2008) [24] and proposed Libyan standards (2016) guidelines for bottled water quality.

Parameter	Units	Range (Measured Values)	Range (Labeled Values)	Mean (Measured)	Mean (Labeled)	Proposed Libyan Standards	WHO (2008)
pH	-	6–8.1	6.5–7.8	7.03	5.4	6.5–8.5	6.5–8
TDS	mg/L	13–122	20–200	69.6	NA	100–500	1000
Na	mg/L	6–32	1.1–80	13.65	12.48	200	200
K	mg/L	0–18	0–2	2.6	0.54	12	200
Mg	mg/L	5–100	0.12–8.5	19.32	1.85	75	150
Ca	mg/L	0–13	0.2–24	1.53	4.01	-	200
Cl	mg/L	0.1–48	0.84–34	20.06	10.87	250	250

Concentration of potassium (K) is at its highest in sample T2 (18 mg/L) followed by sample T7 (6.8 mg/L), while samples T1, T5 and T11 had the lowest (0 mg/L). Potassium is found in the body as the major intracellular cation and its low concentration may lead to glucose metabolism impairment [23]. However, health concerns may be raised regarding the effects of 'potassium-based treatment' of water (i.e., potassium chloride treatment leads to exchange of K with Mg or Ca ions) on high-risk groups (such as individuals with diabetes, hypertension, kidney dysfunction, heart disease, etc.) [25].

The analytical results showed that the chloride concentration varied widely among the different brands investigated in this study (0.1–48 mg/L). However, these concentrations complied with the national and international guideline values of 250 mg/L. On the other hand, Table 1 shows that there is a large difference between the label and actual values. In this case, 29% of the examined bottled water brands did not report the value of Cl^- concentration. WHO [24] has no guideline value for chloride considering its insignificant levels found in drinking water. Excess chloride (>250 mg/L) in drinking water can give rise to noticeable taste [25]. All the brands at the time of the study were therefore expected to have good taste since the chloride levels were well below 250 mg/L.

Among the compositional parameters used in the classification of drinking water, the number of dissolved solids is certainly one of the most important, especially for consumers. On the labels this information is provided by the total dissolved solids (TDS). The results showed that the TDS for bottled water ranges from 13 to 122 mg/L. While the TDS written on labels ranges from 20 to <200 mg/L. The mean value for measured TDS is 69.58 mg/L. Generally, TDS consists of inorganic salts such as calcium, potassium, magnesium, sodium, bicarbonates, sulfates, chloride and also small amounts of organic matter that are dissolved in water.

In this study, among bottled waters, samples T7, T8 and T9 depict a different trend by having a significantly higher value compared to other bottled water. Furthermore, the

values written on the packages varied between 22 and less than 200, and in some bottles the values were missing for unclear reasons, and some bottles did not give clear values. This led to not being able to calculate the mean value. However, results showed that there is a significant difference between measured and labeled TDS values (Table 1).

Bottled waters with a very low-mineral content (TDS < 50 mg/L, 5 samples T1, T3, T5, T10 and T11) are 29% of the waters on the market in Tripoli. This kind of water could be used in hypertension (high blood pressure) for their low sodium content (<10 mg/L) and also have a diuretic effect [26]. An elevated concentration of sodium in the human body by ingestion of bottled water promotes the risk of hypertension and cardiovascular disease [22,23,27]. The results showed that all the analyzed bottled water brands have sodium content that is less than 35 mg/L. Despite the fact that this kind of water could be very suitable to people with hypertension, but it is also far below the maximum recommended limit by national and international standards (200 mg/L). The sodium found in drinking water is responsible for only a small percent of a person's overall sodium intake but is beneficial to retain water in the body.

Concerning bicarbonate, carbonate and sulphate Table 1 shows that about 41%, 23.5%, and 100% of the brands did not report the concentrations of SO_4^{2-}, HCO_3^-, and CO_3^{2-}, respectively, in the water. Table 1 shows that all brands have a SO_4^{2-} concentration lower than 25 mg/L in their labels, while lab measurements showed that SO_4^{2-} concentration ranges from 0 to 10 mg/L. Those states there is a noticeable difference between the two concentrations. SO_4^{2-} is harmless, but it has an effect on the taste of drinking water [25,27,28].

HCO_3^- concentrations ranged from 10 mg/L to 400 mg/L, with a mean of 62.8 mg/L in 94.1% of the brands. The maximum value of HCO_3^- concentration reported by sample T2 (400 mg/L) differs significantly from the value written on the label (34.16 mg/L).

4. Conclusions

The study covers a limited number of bottled waters contained in 0.2 and 0.5 L bottles marketed in the capital Tripoli. In this case, 15 domestic and two imported bottled water brands were analyzed for various physic-chemical water quality parameters. The results showed a widespread in the characteristics of investigated bottled waters, yet the majority met the various national and international bottled water standards for physic-chemical parameters except for pH (5 brands (<6.5)).

Although, most of the analyzed bottled water brands have values less than the maximum limits of the national and international water quality standards, yet there is significant differences between concentration of chemical elements and label insertion on the bottles. Therefore, it is of great importance that all marketed bottled waters be monitored for quality and identity and be licensed by concerned authorities to safeguard consumers' health.

Majority of bottled water brands sold in Tripoli and its suburbs do not have any registration or approved license from public health authorities. This may lead to not having uniform composition and may not always adhere to reported label values, which increases health risks associated with drinking water.

All the investigated bottled waters had commercial brand names, and the expiration dates were labeled, yet the sources of waters were not specified on the labels. The lack of information related to the water source may raise doubts about the quality of water contained in the brands. However, local companies' owners may argue that this kind of information is known for the costumers since the main and only source of water to be desalinated and filled in bottles is groundwater.

5. Recommendations

Enhancing the community's trust in public water supply sources is critical. Municipalities and water authorities can play an important role in this context by introducing an information dissemination program to ensure transparency and accountability as well as awareness campaigns to change misconceptions about the public water quality.

The responsible authorities should form a team to carry out periodic analysis of various local bottled water factories and give this team full power to take appropriate measures when required.

With regard to the environmental aspect, used plastic water bottles should be collected, recycled and utilized into products other than bottles, such as plastic pipe, shopping bags, carpeting, and plastic packaging.

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