

HYDROCHEMICAL FACIERS OF MINERAL WATER AND CLASSIFICATION STANDARDS IN ALGERIA

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Abstract

In this study, we determined the quality and classification of the waters of the various brands of natural mineral waters bottled in Algeria, according to the European and Algerian classification protocol, as well as the Algerian legislative regulations through European standards, and in the light of this analysis, we conclude that the vast majority of mineral waters are of the 91% calcium bicarbonate type and 09% magnesium bicarbonate type, as well as 64% of natural mineral waters in Algeria, sound of waters with a low mineral content and 36% of mineral waters with a medium mineral content.

Keywords: Algeria; mineral water; quality; classification; physico-chemical; bottled.

Introduction

Natural mineral water is a groundwater of underground origin, characterized by the absence of a direct relationship with surface water, geological protection and protection of the environment perfectly stable collected either at source or by drilling [1], it is not subjected to any chemical biological treatment or disinfection [2-3], adequately protect from total contamination when water quality and adequacy are of serious concern due to various waterborne diseases and their adverse effects on human health [4], as well as insufficient data on their occurrence and the potential toxicity of water intended for human consumption, the French Food Security Agency [5-7], it should be noted that natural mineral water is characterized by its stable chemical composition, its (probable) therapeutic properties and its microbiological and pharmacological characteristics, has been made, studies tend to show higher levels of contamination in groundwater intended for human consumption, regardless of the class of compounds considered. When groundwater contains a concentration of certain minerals that exceeds drinking water standards, but it has therapeutic properties it is distributed in bottles with sometimes a well defined treatment, these waters are called mineral waters.

Before bottling, in 2014 the world consumption of bottled water [8], reached 282.8 billion litres, representing an increase of about 9.6% since 2009 [9], since bottled water is also considered a food product, is also regulated, This precious is necessary for the basic survival of all living organisms [10], in the 1990s in Algeria consumption has increased significantly. The bottled water offer has diversified considerably, with no less than forty brands on the market. Small packaging (33cL) is very successful and is developing thanks to out-of-home catering [11]. In Algeria, consumption has evolved in twenty years, from 4L/capita/au in 1989 to 22L/capita/year in 2007, (Fig. 1) [12-14].

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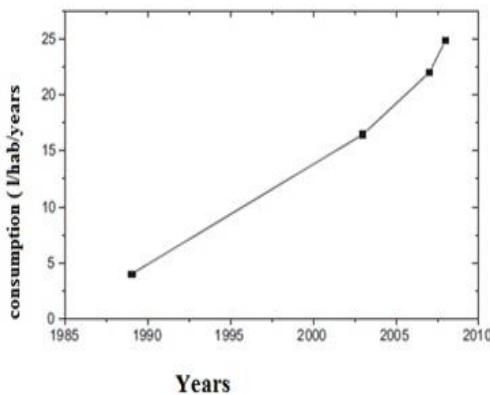


Fig. 1. Evolution of the yearly consumption of mineral water in Algeria [15]

All bottled water products must comply with the standards, in accordance with quality standards, in Algeria the public authority to promulgate a series of regulatory texts aimed at regulating the exploitation, production and marketing of mineral waters [16, 17]. amended and supplemented by Executive Decree N°. 13-298 on the exploitation and protection of natural mineral waters and spring waters, and the overall exploitation rate of the spring and mineral water catchment fields in Algeria reached 699 liters per second (l/s), or $60.394\text{m}^3/\text{day}$, the selection protocol implemented has made it possible to declare more than twenty sites as natural mineral waters (Fig. 2) [15].

The objective of this study was to evaluate the quality of bottled mineral water on the Algerian markets, Algerian legislative regulations through European standards, as well as the classification of all brands of bottled mineral water in Algeria.

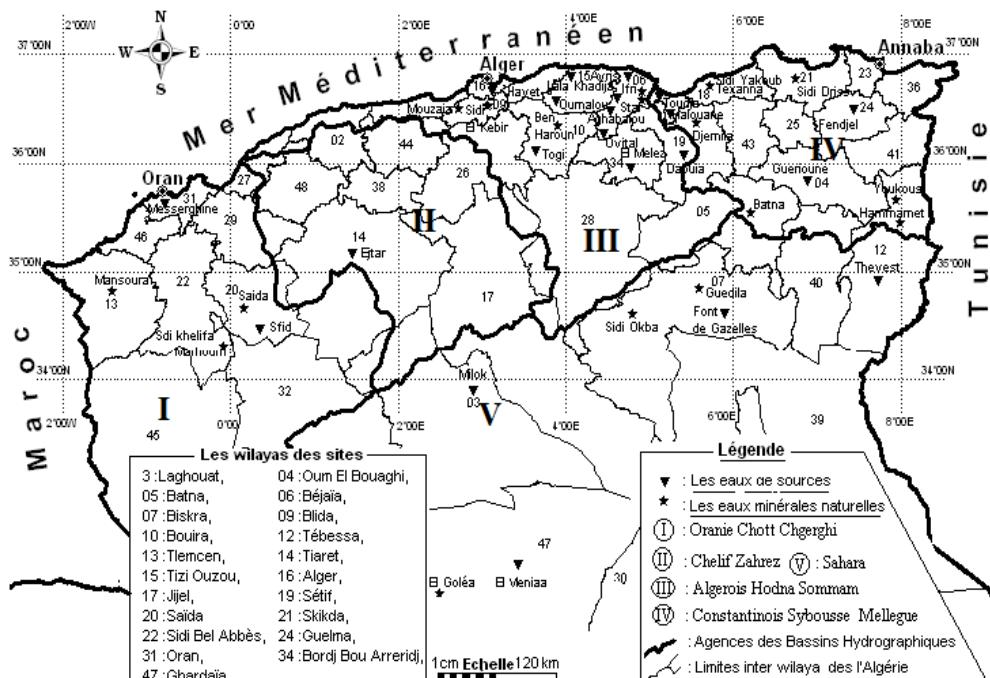


Fig. 2. Distribution of mineral and spring water sites in Algeria [15]

Geography of the operating sites

According to the regions, figure 2, give the geographical indications and distribution concerning the sites of mineral waters and those of spring waters in Algeria, we note that the central region are produced more than 40% of the brands, in -east, 32.43% in east, and 16.22% in west of the country, or slightly more than 89%, the brand Tazliza in south of the country (Adrar).

The brands produced and distributed are composed of 17 spring waters, one of which is carbonated (Cordial) and 20 brands of natural mineral water, two of which are carbonated (Mouzaïa and Ben Haroun). All sites are codified according to the nature of the water, the locality and the watershed to which they belong. Twenty-seven percent of the mineral water sites are located in the Algiers-Hodna-Soummam basin and 36% in the Constantinois-Seybousse-Mellegue basin, at the level of the Algiers-Hodna-Soummam basin represents 53% of the spring water, and 88% of all sites are located in the north [15].

Material and methods

Sample collection and analysis

Twenty-two samples of bottled mineral water were taken, in different grocery stores in the Algerian markets, the most commercialized and consumed. Each sample presented one bottle of mineral water with a capacity of 1.5L, for each registered brand, thus were used to analyze the selected parameters: Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , K^+ , SO_4^{2-} , HCO_3^- , NO_3^- , NO_2^- , PH, F and dry residues.

For the pH determination, pH meters (Orion 4 stars) were used. Chloride (Cl^-) was determined by titrimetry [18]. Sulphate (SO_4^{2-}) and nitrate (NO_3^-), nitrite (NO_2^-) were measured using the UV-VIS spectrophotometer (Shimadzu 3401) The metal contents in the form of ions (N^+ , Ca^{2+} , K^+ , HCO_3^- and Mg^{2+}) were determined by atomic absorption spectrophotometer (Shimadzu AA-6800) using an air/acetylene flame, and the Cl^- anion is measured by the MOHR method called "argentometry", chlorine is precipitated by titrated silver nitrate in the presence of chromate.

Graphical data processing

The Piper and Schöeller diagrams were used to show the nature of the relationship between the groups, using the different hydrochemical parameters. These stables were used to determine the origin of natural mineral waters, on the other hand were used the Stabler method, which consists in classifying anions and cations separately in order of decreasing values, and thus determining the chemical facies.

Statistical analysis

The collected miniral water physicochemical data (Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , K^+ , SO_4^{2-} , HCO_3^- , NO_3^- , NO_2^- , PH) were assigned to geo-coordinates and exported to a SURFER domain (SURFER32 software, 2010 geostatistical analysis). For carrying out statistical analysis of the obtained data's of the mineral waters, a correlation was developed between the parameters by applying Karl Pearson's coefficient of correlation. MS Excel was used to find out the Min, Max, Mean, Standard deviation (SD), coefficient of variation (CV) and Skewness (SK) of the data's.

Results and Discussion

Classification of mineral water

In nature, there is no upper or lower limit for mineral contents in natural mineral water [19], and to classify water types, specialized researchers have developed several hydrochemical classification systems, in this case, the legislation applied in Algeria until January 2006, reflect the public authorities' desire to bring the entire regulatory framework up to international

standards [16, 20]. Classification systems have also been used to identify such multitudes and/or chemical differences between water marks. The Algerian mineral water directives for chemical composition criteria are presented in table 1. This legal arsenal reflects a concern for the public health of consumers, the quality and health of life of populations. The standards adopted for each physical, physico-chemical and microbiological characteristic are thus determined in accordance with the recommendations of international health standards and those of proven experience in water treatment and marketing. We will mention here (Table 1) some of the standards set by the Algerian legislator, although this Algerian legislation does not define the bicarbonate content despite its great importance, nor the "silica" content, and according to the European mineral water directive, table 2 shows the classification of the data currently observed for bottled water, and in accordance with European legislation [2], use to establish a classification of the different mineral waters based on the analysis of the main parameters, therefore natural mineral waters are classified by the fixed residue at 180°.

On the other hand, the table 3 shows the classification of natural mineral waters on the basis of their mineral chemical facies, the role and effects of mineral waters of each type [21], on the sanitary properties [22] have also been studied. In this sense, it is noted that the fluorine concentration on the labelling of bottled water does not exceed 0.5mg/L, and in cases where the content exceeds 15mg/L according to Algerian regulations, the producer is obliged to indicate on the labelling of the bottles that this water is not suitable for consumption by children under 3 years of age [23].

Table 1. Quality indicators for natural mineral waters (Algerian standards)

Characteristics Toxic and undesirable substances	Maximum permissible concentration according to the standards (mg/L) Symbol	Algerians (Inter-ministerial decree of 22 January 2006)
Antimony	Sb	0.005
Arsenic	As	0.05
Barium	Ba	1.00
Borates	BO ₃	5.00
Cadmium	Cd	0.003
Chromium	Cr	0.05
Copper	Cu	1.00
Cyanure	CN	0.07
Fluorure	F	5.00
Lead	Pb	0.01
Manganese	Mn	0.10
Mercury	Hg	0.001
Nickel	Ni	0.02
Nitrates	NO ₃	50.00
Nitrites	NO ₂	0.02
Selenium	Se	0.05

Table 2. Classification European of natural mineral waters based on fixed residue at 180°C (2009/54/EC Directive) [24]

Fixed residue at 180°C	Definition
< 50mg/L	Very low mineral content water (or light mineral water)
50-500mg/L	Low mineral content water
500-1500mg/L	Medium mineral content water
> 1500mg/L	Rich mineral content water

The anions

The analysis values of the SO₄²⁻ ion, were between maximum 514mg/L and minimum 10mg/L, their average value 68.18mg/L and CV equal 1.50. chloride, their values between maximum 400mg/L and 0.5mg/L minimum, with average value 65.02mg/L and CV equal 1.25.

The concentration of bicarbonate ions is between 1809mg/L and 27mg/L, and an average of 346mg/L, and CV equal to 1.01, the concentration of nitrate ions, between 14mg/L and 0.0mg/L, with an average of 4.11mg/L and CV equal to 1.13, the nitrite, their values between 05mg/L and 0.0mg/L, their maximum and minimum 0 mg/L, with an average of 0.52mg/L and CV equal to 2.70.

In this analysis notes that bicarbonate ion and sulphate ion are the most dominant in mineral water brands in Algeria (Tables 4 and 5, Fig. 3).

Table 3. Characteristics of the main natural mineral waters and their respective general therapeutic indications

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

Table 4. Descriptive of the measured bottled mineral water physicochemical properties in Algeria

Springs	Year	Anion concentration in mg/L						Cation concentration in mg/L				dry residues mg/L	
		SO ₄ ²⁻	Cl ⁻	F ⁻	HCO ₃ ⁻	NO ₃ ⁻	NO ₂ ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺		
Benharoun	2012	514	400	-	1809	-	0.2	413	63	680	10	6.7	2800
Mouzaia	2012	79.1	135	-	811.3	7.10	0.0	133.6	77.28	--	2.55	7.08	620
Guedila	2012	171	73	-	317	0.00	0.7	97	47	47	01	7.1	712
Mansoura	2012	60	90	0.15	397	-	-	89	62	30	01	7.2	640
Chifaa	2012	40	48	-	263	-	11.0	66	26	15	02	7.2	608
Messereghine	2012	35	128	0.2	331	-	-	63	41	63	08	7.3	577
Sidi Yakoub	2012	32	65	-	226	-	-	83	14	37	4.9	6.5	560
Saida	2012	68	85	-	390.4	11.00	0.0	77.20	50.6	--	3.1	7.44	544
Djamilia	2012	45	28	-	354	-	0.0	112	24	20	11	7.5	468
Batma	2012	29	18	-	373	-	0.0	58	43	13	3.1	7.2	450
Sidi okba	2012	75	55	-	213	5.26	0.0	83	18	30	21	7.3	425
Ifri	2012	52	74	-	305	14.00	0.0	93.8	26.04	--	2.0	7.0	360
Daouia	2012	19	41	0.5	280	-	0.4	32	20	75	07	7.8	325
Sidi Elkebir	2012	21	22	-	230	4.80	0.0	55	11	34	0.5	0.7	297
Fendjel	2012	24	0.5	-	244	-	15.0	73	15	12	2.5	7.9	268
Toudja	2012	21	71	-	212	0.02	0.0	61	14	52	0.8	7.4	248
Hammamet	2012	29	21	-	209	0.01	0.5	63	15	13	4.4	7.4	238
Youkous	2012	27	21	-	216	-	0.3	67	10	12	4.9	7.4	231
Sidi driss	2012	10	17	-	27	0.02	0.1	39	03	7.2	0.1	7.7	202
Lalla khedidja	2012	32.88	08	0.2	201.3	0.50	0.0	54.8	7.68	05	05	7.2	187
Milouk	2012	80	10	0.4	85	-	0.0	53	12	08	04	7.6	180
El goulia	2012	36	20	-	118	2.50	0.0	24	07	28	05	7.4	180

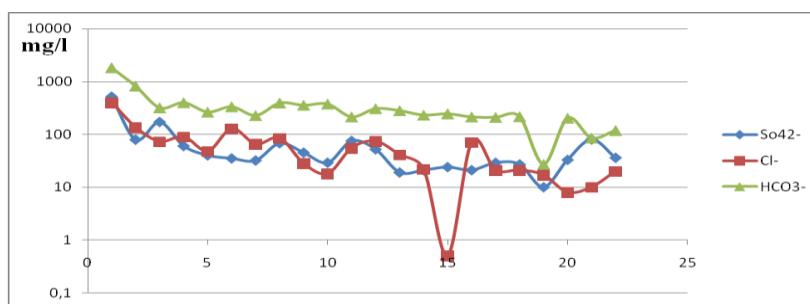


Fig. 3. Profile of concentrations of SO₄²⁻, Cl⁻ and HCO₃⁻ in mineral waters bottled in Algeria (logarithmic scale)

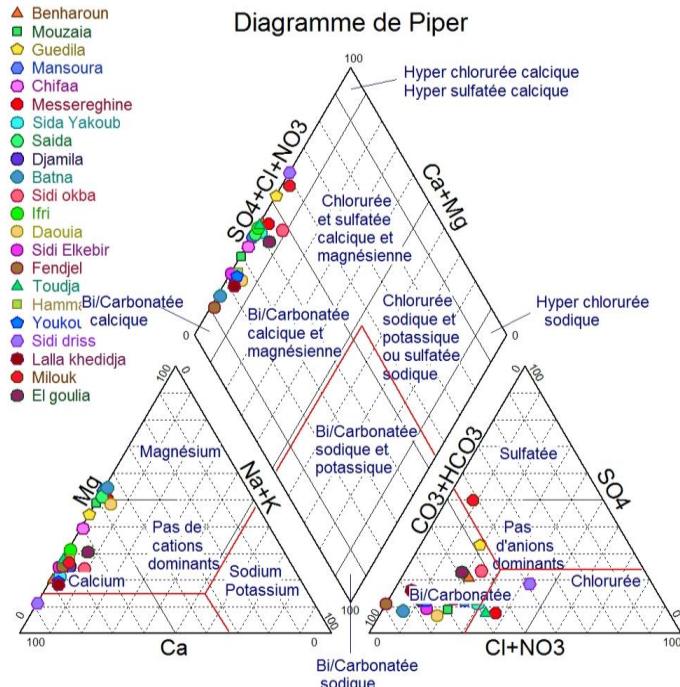


Fig. 4. Quality of Algerian mineral waters on the Piper diagram

The cations

The calcium cation analysis shows values between maximum 133.6mg/L to minimum 24mg/L and an average of 71.03mg/L, CV equal 0.40, the magnesium cation concentration, between maximum 63mg/L to minimum 0.3mg/L, an average of 23.82mg/L and CV equal 0.75.

The sodium values between maximum 680mg/L and minimum 05 mg/l, with an average of 62.16mg/L and CV equal 2.36, as well as the potassium cation analysis between maximum 21mg/L and minimum 0.1mg/L, with an average of 5.06mg/L and CV equal 0.95.

The pH, values were between maximum 7.9 and minimum 6.5, with an average of 7.29 and CV equal to 0.043, we notice that 86% have a pH greater than 7, at the dry residue analysis level by registering values between maximum 2800mg/L to minimum 180mg/L, with an average of 505.45 mg/L and CV, equal 1.04 (Fig. 5)

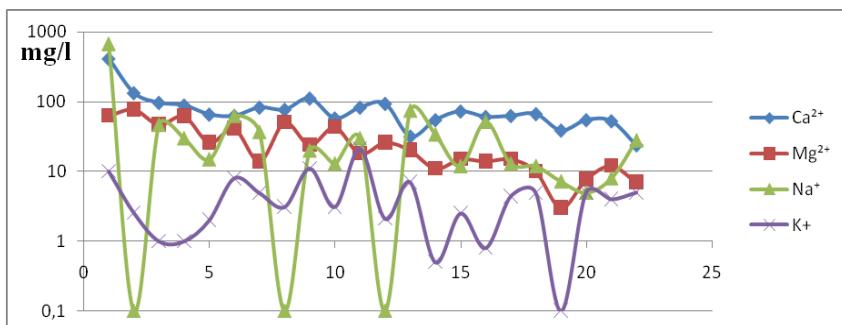


Fig. 5. Profile of concentrations of Ca^{2+} , Mg^{2+} , Na^+ and K^+ in mineral waters bottled in Algeria (logarithmic scale)

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Table 5. Descriptive statistics of the measured bottled mineral water physicochemical properties in Algeria

Description	SO_4^{2-}	Cl^-	HCO_3^-	NO_3^-	NO_2^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	pH	dry residues mg/L
Min	10.00	0.5	27.0	00.0	00.0	24.0	0.3	0.5	0.1	6.5	180.0
Max	514.0	400.0	1809	14.00	0.50	133.6	63.00	680	21.00	7.9	2800.0
Mean	68.18	65.02	346.0	4.11	0.52	71.03	32.82	62.16	5.06	7.29	505.45
Standard deviation (SD)	102.90	81.83	352.17	4.65	1.42	28.93	17.86	146.89	4.83	0.31	528.37
CV%	1.50	1.25	1.01	1.13	2.70	0.40	0.75	2.36	0.95	0.043	1.04
Skewness	3.69	3.06	328.00	0.89	2.75	0.48	1.03	3.89	1.82	-0.40	3.65

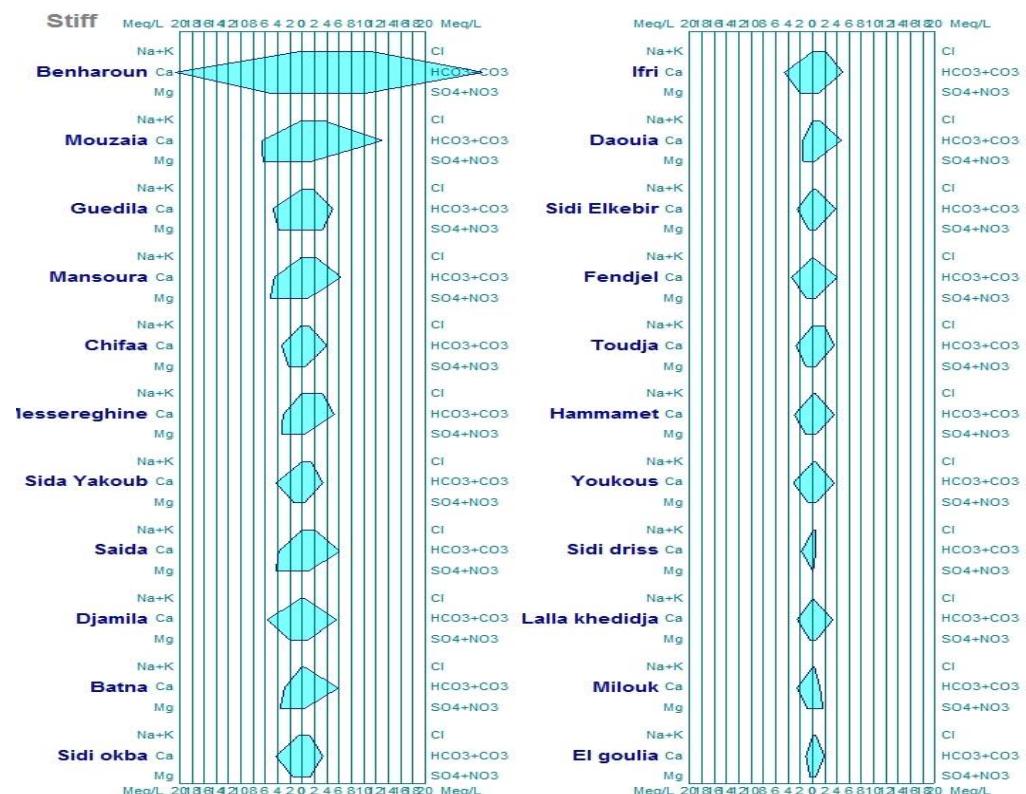


Fig. 6. Quality of Algerian mineral waters on the Stiff diagram

We can distinguish in the light of this analysis that the cations Ca^{2+} , Mg^{2+} and Na^+ the most dominant, as well as the representation of mineral water analysis data in Algeria on the piper diagram and the Stiff diagram, indicates that there is little diversity (Fig. 4 and Fig. 6), and according to Stabler's classification the vast majority of mineral waters are of the type 91 % calcium bicarbonate, and 09% magnesium bicarbonate (Fig. 7). The classification protocol used for this study refers to European standards [2]. This protocol is systematically applied to mineral water classifications [25-30] and seems to be more consensual [31].



Fig. 7. Quality of Algerian mineral waters on the Stabler diagram

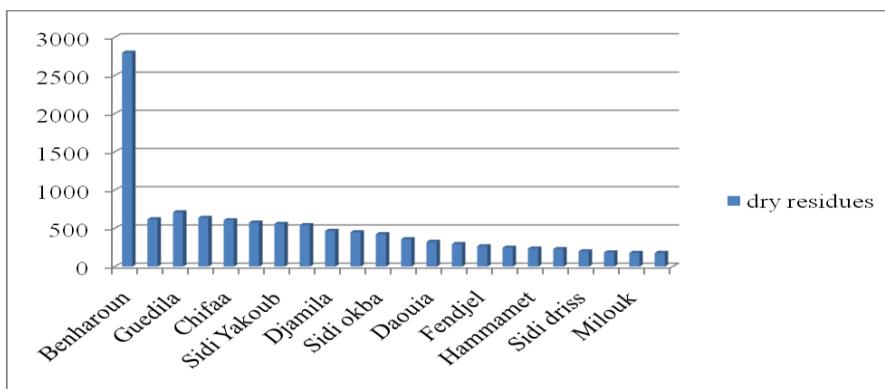


Fig. 8. Classification of natural mineral waters according to the European standard [2]

According to the European classification of natural mineral waters based on fixed residues at 180° [24-26], figure 8 indicates that bottled natural mineral waters are 100% above the 50mg/L threshold of the dry residue, and we concluded that 64% of natural mineral waters in Algeria, which are low mineral waters, are bottled brands, Djamila, Batna, Sidi okba, Ifri, Daouia, Sidi Elkebir, Fendjel, Toudja, Hammamet, Youkous, Sidi driss, Lalla khedidja, Milouk and El goulia. and on the other hand, the concentration values of dry residues, shows that 36% of mineral waters with a medium mineral content, these are the brands, Benharoun, Mouzaia, Guedila, Mansoura, Chifaa, Messereghine, Sidi Yakoub and Saida.

Conclusion

This work allows a better evaluation of the different brands of bottled mineral waters and of the hydrochemical processes on the quality of mineral waters in Algeria, to pursue the scientific and legislative policies for the protection of bottled mineral waters, hot springs, contamination by PFAS and pesticides [31-32].

This comparative study provides technical criteria for the qualification of waters between on the one hand the provisions of the Algerian legislation, and on the other hand the European legislation as well as the physico-chemical characterization. In the light of this analysis, and in relation to the difference in legislation, we conclude that the vast majority of mineral waters are of the type 91% calcium bicarbonate and 09% magnesium bicarbonate, as well as 64% of natural mineral waters in Algeria, the noise of waters with low mineral content and 36% of mineral waters with medium mineral content, and can help consumers to better understand the nature, quality and importance of this water, and healthy and environmentally friendly.

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