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ASSESSMENT OF WATER QUALITY OF BLIDA'S WATER TOWERS AND DETERMINATION OF TRIHALOMETHANES BY GC METHOD COUPLED TO HEADSPACE

BENAROUS Mohamed El Amine¹, HAMAIDI-CHERGUI Fella¹*, CHAIBI Zineb¹ et HARRAOUI Samir²

1. Biotechnology-Environment and Health laboratory, faculty of SNV, Department BPC, University of Blida 1 PB270 Blida (09000), Algeria 2. Central laboratory of water quality, Algerian waters 48 Daib Aissa, Bordj El-Kiffan Algiers (16000), Algeria

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Abstract

Description of the subject: in Algeria, water chlorination is the most widely used disinfection method to reduce the incidence of waterborne diseases and ensure good quality water for the population without health risk, however the reaction between chlorine and organic matter present naturally in water causes the formation of by-products of disinfection, among these by-products one finds in particular the Trihalomethanes, according to some toxicological research which have a carcinogenic potential.

Objective: in this context, we have chosen to study the water quality of water towers intended for the supply of drinking water at for cities of the Wilaya of Blida (50 Km from Algiers).

Methods: Water samples were subject of physicochemical analysis. The determination of Trihalomethanes in water was carried out by gas chromatography method coupled to Headspace .

Results: The physicochemical analyses in the water of Blida showed values between 12.5 °C and 25.2 °C for the temperature; of 7.28 and 8.15 for the pH; of 0.08 and 1.04 mg/L for oxidability; of 0.12 and 1.34 mg/L for total organic carbon), and levels between 0 and 0.7 mg/L of chlorine. The obtain results of the Trialomethanes determination showed concentrations less than 5 μ g/L for the four parameters of Trihalomethanes

Conclusion: The water distributed in the different cities of Blida does not contain THM, so there is no health risk associated with THMs.

Keywords: Chlorination; Disinfection; Organic matter; Reservoirs; Trihalomethanes.

ÉVALUATION DE LA QUALITÉ DES EAUX DES CHATEAUX D'EAU DE LA WILAYA DE BLIDA ET DÉTERMINATION DES TRIHALOMÉTHANES PAR MÉTHODE DE LA CPG COUPLÉE AU HEADSPACE (ESPACE DE TÊTE STATIQUE)

Résumé

Description du sujet: En Algérie, la chloration de l'eau est le procédé de désinfection le plus utilisé pour réduire l'indice des maladies hydrique et assurer une eau de bonne qualité pour la population et sans risque pour la santé. Toutefois, la réaction entre le chlore et la matière organique présente naturellement dans l'eau entraine la formation de sous-produits de désinfection toxiques (SPD). Parmi ces SPD, on retrouve notamment les Trihalométhanes (THM) qui possèdent un potentiel cancérogène selon certaines études toxicologiques.

Objectif: C'est dans ce contexte que nous avons choisi d'étudier la qualité de l'eau des châteaux d'eau destinée à l'alimentation en eau potable dans quatre villes de la Wilaya de Blida (50 Km d'Alger).

Méthodes : Les échantillons d'eau ont fait l'objet d'une analyse physico-chimique. La détermination des trihalométhanes dans l'eau a été réalisée par chromatographie en phase gazeuse couplée au Headspace.

Résultats : Les analyses physico-chimiques dans l'eau de Blida ont montré des valeurs comprises entre 12,5 ° C et 25,2 ° C pour la température, de 7,28 et 8,15 pour le pH, de 0,08 et 1,04 mg / L pour l'oxydabilité, de 0,12 et 1,34 mg / L pour le carbone organique total et des taux de chlore variant entre 0 et 0,7 mg / L.

La détermination des Trihalométhanes dans les eaux des réservoirs de la wilaya de Blida par analyse par la chromatographie en phase gazeuse et par la méthode espace de tête montre une concentration inférieure à 5 μ g/L pour les quatre paramètres de Trihalométhanes.

Conclusion: L'eau distribuée dans les différentes villes de la Wilaya de Blida ne contient pas de THM, de ce fait cette eau ne représente pas de risques pour la santé humaine dus aux THM.

Mots clés : Chloration ; Désinfection ; Sous-produits, Matière organique; Réservoirs ; Trihalométhanes.

*Auteur correspondant: HAMAIDI-CHERGUI Fella, E-mail : hamaidifella@yahoo.fr

Chlorine disinfection plays a predominant role in ensuring good microbiological quality of drinking water. This is the reason why this practice has become more and more common since the beginning of the 20th century [1]. It has led to a massive reduction in waterborne diseases such as typhoid and cholera.

Chlorine, chloramines, chlorine dioxide, ozone and iodine are the most frequently used substances in the process of disinfection of water [2]. Chlorine persists for a long time in the water as residual chlorine minimizing the possibility of contamination by microbes between the water treatment plant and the tap [3], on the other hand, it has certain disadvantages, the main one being related to the formation of chlorinated by-products. The most important are Trihalomethanes [4].

Trihalomethanes are volatile organic compounds containing one carbon atom, one hydrogen atom and three halogen atoms, namely chlorine, bromide or iodine. The main Trihalomethanes are Chloroform formed (CHCl₃) which accounts for the highest proportion of this family [5], Bromodichloromethane (CHCl₂Br), Dibromochloromethane $(CHBr_2Cl)$ and Bromoform $(CHBr_3)$. Trihalomethanes represent 30% of the total halogenated organic compounds [6].

Chlorine and organic matter are not the only parameters that react with the formation of THM. The parameters affecting the variability of THM concentration in drinking water can be grouped into two groups: raw water quality parameters (organic matter and bromide ions) and operational parameters (temperature, pH, chlorine dose and contact time).

Drinking water is the most important source of exposure for Trihalomethanes, they are also found in drinks made with treated water, a US study of soft drinks showed that concentrations ranged between 3.2 μ g/L and 44.8 μ g/L for total THM [7], chloroform was present in some toothpastes, ointments and cough syrups. Dermal and respiratory THM exposure can also be very important given their volatile and lipophilic character. Taking a bath or shower, bathing in a pool, washing dishes are all activities exposing individuals to THM by dermal and inhalation [8].

Toxicological studies showed that the presence of THM in drinking water can causes cancer in laboratory animals. In 1976, it was observed that chloroform could cause tumours in the liver and kidneys in mice orally [9]. At low doses, chloroform induces tumours in the kidneys but not in the liver in rats [10], Bromodichloromethane can cause tumours in the large intestine as well as kidney [11]. tumours in rats and mice Dibromochloromethane would produce liver and kidney damage for prolonged exposure at high doses [12] as for the Bromoform it would cause, in large doses, tumours in the large intestine in the rats but not to the mice [13].

Epidemiological studies show an increased risk of bladder cancer due to drinking water consumption [14], other studies have focused on the effects of exposure to THM on reproduction and development. There appears to be a link between exposure to THM and spontaneous abortion [15]. Other studies show a relationship between by-products of disinfection exposure and birth weight stunting, neural tube defects and labio-palatal fissures [16].

Two studies on Trihalomethanes were carried out in Algeria, Achour and Guergazi's works in 2002 on the impact of water mineralization on the reactivity of organic compounds with chlorine in Drauh and oued Biskra, Ifri, Youkous, showed a significant impact of pH and contact time of chlorine on the reactivity of organic compounds and chloroform is formed in appreciable quantity in water which do not contain bromide ions, a formation of chlorinated derivatives that brominated with a variable distribution of the different Trihalomethanes according to the mineral characteristics of these waters.

Another recent study of Benhamimed and Moulessehoul published in 2017 on the and presence seasonal variation of Trihalomethane in Mostaganem's drinking water, the study was conducted on three regions of the city and shows a high concentration of Dibromochloromethane and Bromoform, this confirms the high content of bromide ions in drinking water sources, a maximum value (198 µg/L) of THM was recorded in July and a minimum value (6.94 µg/L) in the month of December.

It is in this context that we have chosen for the first time to study the water quality of water towers intended for the supply of drinking water at the wilaya of Blida.

MATERIALS AND METHODS

1. Collect of samples

The sampling sites are five water towers located in the wilaya of Blida (water tower of the Feroukha water treatment plan, Soumaa), (water tower of the public hospital of Frantz Fanon, Blida center), (water tower of the city Beni-mouimen, El-Affroun), (water tower of Bouhassen, Mouzaia), (water tower of Hai Nadjah, Chiffa). The sampling was carried out from February to May 2017 with one sampling every 15 days. The analyzes of the water samples taken were carried out at laboratories of the Algerian waters (ADE). Sampling is done manually and stored immediately in a cooler with a temperature below 4°C. Each sample was subjected to:

-Physico-chemical analyses at Algerian waters (ADE) laboratory unit of Chiffa-Blida-Algeria. The samples are taken in 500 ml flasks.

-Analysis of the four parameters of Trihalomethane (chloroform, bromodichloromethane, dibromochloromethane and bromoform) at the central laboratory of the Algerian waters (ADE) Bordj Elkifan-Algiers-Algeria. The samples are taken in sterile 250 ml flasks with the addition of sodium thiosulfate and covered with aluminum foil to inhibit light penetration.

The evaluation of the water quality of the water towers and determination of Trihalomethanes are carried out by analysis of physico-chemical parameters (Table 1).

Table 1 : Procedures used for the analysis

Parameters	Standards
Temperature	Digital thermometer
Hydrogen potential (pH)	NA75/1990
Oxidability	ISO 8467 / NA 2064
Total Organic Carbon (TOC)	ISO 8245
Dose of chlorine	DPD No. 1 method
Trihalomethanes	ISO 10301

2. Dosage of Trihalomethanes (THM)

The four parameters of THM are measured by Headspace method and analysis with gas chromatography according to ISO 10301. The samples are taken from sealed vials in which the ration of volume of water withdrawn and volume of air is fixed. The temperature of the flasks is maintained between 50°C and 80°C in a thermostatic system in order to be placed in equilibrium conditions. Chromatographic analysis of the gas phase in equilibrium with the water in the sampling flasks is carried out using an Electron Capture Detector (ECD). The operating mode is as follows :

2.1. Temperature stabilization of samples

Place the sample vials in the thermostatic system at a fixed temperature between 50°C and 80°C for at least 30 min and for an equal time for all vials.

2.2. Gas chromatography (Perkin Elmer clarus 680)

Set the chromatograph equipped with an electron detector (ECD) according to the manufacturer's instructions.Eliminate any possibility of contamination of the ECD which could lead to an elevated or irregular baseline.Inject an aliquot portion of gas into the chromatograph column. Compare the chromatogram obtained with those of the calibration solutions.

2.3. Blank determination

Prior to analysis and between analyses, carry out blank tests by applying the complete protocol with THM-free water (we used a commercialized source water "Guedila").

2.4. Calibration

This analysis requires calibration over the entire procedure, this is done by preparing aqueous solution of the compounds to be determined in an individual concentration range located in the linear dynamic range of the detector. Dimethylformamide, acetone or methanol can be used as water-miscible solvents; these solvents provide a fast distribution of halogenated hydrocarbons in the water.

2.5. Preparation of the $10.10^4 \mu g/l$ intermediate solution

In a volumetric flask of 5 ml, introduce 100 mg of the 2000 μ g/L standard solution with a micro syringe and make up to the mark with methanol, this solution is stable for 4 months stored in the dark and at 4°C.

2.6. Preparation of standard solutions for the calibration curve

In a 5 ml graduated flask, add 50 μ l of the 10.10⁴ μ g/l standard solution and make up to the mark with water, this solution is noted standard N°1 with concentration of 1000 μ g/L.

In another 5 ml vial, add 100 μ l of the 10.10⁴ µg/l standard solution and make up to the mark with water, this solution is noted standard N°2 with concentration of 2000 µg/L. In another 5 ml graduated flask, add 200 μ l of the 10.10⁴ µg/l standard solution and make up to the mark with water, this solution is noted standard N°3 with concentration of 4000 μ g/L. In another 5 ml vial, add 450 μ l of the 10.10⁴ μ g/l standard solution and make up to the mark with water, this solution is noted standard N°4 with concentration of 9000 µg/L. In another 5 ml vial, add 550 μ l of the 10.10⁴ μ g/l standard solution and make up to the mark with water. this solution is noted standard N° 5 with concentration of 11000 µg/L.

2.7. Calibration curve

Take 100 μ l of each solution 1,2,3,4 and 5 using a micropipette and place in 10 ml vials and top up with water, concentrations have become 10 μ g/L, 20 μ g/L, 40 μ g/L, 90 μ g/L, 110 μ g/L. Take 5 ml of each solution using a carefully rinsed pipette after each use and put in a vial, place the metal cap and close well. The calibration curve is established following the working instruction of the equipment.

2.8. Sample

Take 5 ml of the sample using a pipette and put it in vial.

2.9. Expression of results

The results are given in micrograms per liter (μ g/L).

3. Statistical study

We applied the Principal Component Analysis method (PCA) to visualize the water quality of the five water towers in order to process the data table, we used the XLSTAT 2017 software.

RESULTS AND DISCUSSION

The results carried out from February to May 2017 are compared to the standards recommended by the Official Journal of the Algerian Republic (JORA, 2011; JORA, 2014).

1. Temperature

During the study period, the results are shown in Fig. 1. The temperature values range from a minimum of 12.5°C to a maximum of 25.2°C. These values are based on sampling time and weather conditions. In Algeria, executive decree No. 11-125 of 22 March 2011 on the quality of water for human onsumption sets an indicative value of 25°C.

The values observed in this study for the different samples are below this indicative value of JORA, with the exception of one sample that exceeds with 25.2 °C, this increase is due mainly to weather conditions on the day of collection.



Figure 1: Temperature variations in water samples

2. pH

In this study, the results obtained (Fig. 2) shows that the pH values are between 7.28 and 8.15. Executive decree No. 14-96 of 4 March 2014 amending and supplementing decree No. 11-125 of 22 March 2011 on the quality of human consumption water mentions an indicative value for pH $\ge 6.5 \le 9$. From the obtained results, it can be seen that the pH values for the various samples of water are very close to neutrality.



Figure 2: pH variations in water

3. Oxydability

The analysis of organic matter by the oxidability of permanganate of potassium shows that the waters studied contain low concentration of organic matter. The values obtained ranged between 0.08 and 1.04 mg/l of oxygen (Fig. 3).

Executive decree No. 11-125 of 22 March 2011 on the quality of water for human consumption sets a limit value of 5 mg/l. The values obtained during this study do not exceed the limit value fixed by the decree.



Figure 3: Oxydability values of potassium permanganate

4. Total organic carbon (TOC)

The results of the total organic carbon analysis indicate that the organic matter concentration is very low in the studied waters, with values varying between 0.12 and 1.34 mg/l of carbon (Fig. 4). The Official Journal of the Algerian Republic did not mention a limit or indicative value for this parameter. The French standard for water intended for human consumption public health code article R-1321-1 to R-1321-66 and annexes 13-1 to 13-3 indicates a value of 2 mg/l of carbon. The TOC values obtained do not exceed the value set by the French standard.



Figure 4: TOC values in water samples

5. Chlorine

On the basis of the data shown in Fig. 5, it can be seen that the chlorine contents vary between 0 and 0.7 mg/l. Decree NO. 11-125 of the Official Journal of the Algerian Republic indicates a chlorine limit value of 5 mg/l.

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Environmental Protection Agency (EPA) requires that the residual disinfectant concentration must be at least 0.2 mg/l in the water entering the distribution system and that chlorine is detectable throughout the distribution system. According to the World Health Organization, a residual concentration of chlorine is between 0.2 and 0.5 mg/l. According to the Algerian standard, the chlorine content in the water towers does not exceed the value indicated in the decree. But in some samples, a total absence of residual chlorine 0 mg/l was noted, this could be due to problems with the automatic chlorine injector.





6. Trihalomethanes

There are various analytical techniques for the determination of Trihalomethanes. In this study we used the gas chromatography method coupled to Headspace with Electron Capture Detector (ECD), detection limits of this method is 5 μ g/L. Executive decree No. 14-96 of 4 March 2014 amending and supplementing decree No. 11-125 of 22 March 2011 on the quality of water for human consumption mentions a limit values for the four THMs (Tab. 3):

Table 2: Limit values for THMs

THMs	Values	Unit
Chloroform	200	μg/L
Bromoform	100	μg/L
Dibromochloromethane	100	μg/L
Bromodichloromethane	60	μg/L

The results obtained are illustrated in Table 3. We can see that the four THM compounds (Chloroform, Bromoform, DBCM and BDCM) comply with the limit values set by the decree.

BENAROUS et al. Table 3: THMs results

Samples	THM	Soumaa	Frantz	Affroun	Mouzaia	Chiffa
1st	Chlorof	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
	orm	μg/L	μg/L			
sample	BDCM	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
		μg/L	µg/L			
20/02/20	DBCM	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
17		μg/L	μg/L			
	Bromof	< 5	< 5	$< 5 \ \mu g/L$	$< 5 \ \mu g/L$	$< 5 \ \mu g/L$
	orm	μg/L	μg/L			
2 nd	Chlorof	< 5	< 5	$< 5 \ \mu g/L$	$< 5 \ \mu g/L$	< 5 µg/L
	orm	μg/L	µg/L			
sample	BDCM	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
		μg/L	μg/L			
07/03/20	DBCM	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
17		µg/L	µg/L			
	Bromof	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
	orm	μg/L	μg/L			
3 rd	Chlorof	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
. –	orm	µg/L	µg/L			
sample	BDCM	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
	DDCI	µg/L	µg/L			
14/03/20	DBCM	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
1/	D (μg/L	μg/L			
	Bromof	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
4.41	Orm Chilere f	μg/L	μg/L	· 5 · /1	· 5 · /I	. Г / Т
4 th	Chlorof	< 5 	< 5 	< 5 µg/L	< 5 µg/L	< 5 µg/L
		μg/L	μg/L	< 5	< 5 ~/I	< 5
sample	BDCM	C > برمال	5 > برمال	< 5 µg/L	< 5 µg/L	< 5 µg/L
02/04/20	DPCM	μg/L	μg/L	< 5 ug/I	< 5 ug/I	< 5 ug/I
17	DDCIVI	Ug/I	LIG/I	< 5 µg/L	< 5 µg/L	< 5 µg/L
17	Bromof	μg/L 5	μg/L 5	< 5 µg/I	< 5 µg/I	< 5 µg/I
	orm	Ug/I	ug/I	$< J \mu g/L$	< 5 μg/L	< 5 µg/L
5 th	Chlorof	μg/L 	μg/L 5	< 5 µg/I	< 5 µg/I	< 5 µg/I
5 11	orm	ц <u>я</u> /І	ц <u>я</u> /I	< 5 µg/L	< 5 μg/L	< 5 µg/L
sample	BDCM	μ <u>σ</u> /L < 5	μ ₆ /.L < 5	< 5 µg/I	< 5 µg/I	< 5 µg/I
sample	bbem	τισ/Ι.	πσ/Ι	< 5 µg/L	$< 5 \mu g/L$	< 5 µg/L
17/04/20	DBCM	 < 5	<u>μ₆, Ε</u> < 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
17	DDem	ц <u>о/</u> Г.	цσ/Г.	< 5 µg/L	< 5 µg/L	< 5 µg/L
	Bromof	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
	orm	ug/L	ug/L	(0 µg/1	(0 µg/L	(5 µ8/ E
6 th	Chlorof	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
0 til	orm	ug/L	ug/L	10 48 2	10 48 2	10 48.2
sample	BDCM	< 5	< 5	< 5 µg/L	< 5 µg/L	< 5 µg/L
sumpre	22011	ug/L	ug/L	10 48 2	10 48 2	10 48.2
08/05/20	DBCM	< 5	< 5	< 5 ug/L	< 5 ug/L	< 5 ug/L
17	22011	ug/L	ug/L	10 MB 2	10 mg 2	- mg -
	Bromof	< 5	< 5	< 5 ug/L	< 5 ug/L	< 5 ug/L
	orm	ug/L	ug/L	10 MB 2	10 mg 2	- mg -
		r:o -	r:o =			

7. Statistical study

The statistical treatment of PCA was carried out with the PEARSON coefficient on 5 reservoirs and 6 parameters: Hydrogen potential, residual chlorine, temperature, total organic carbon, oxidability of permanganate of potassium and Trihalomethanes. A typological approach of the different variables (F1 and F2) according to their affinities and grouping is presented in Fig.6. It is the interpretation of these graphs that will allow us to understand the structure of the data analyzed.





The variables most closely correlated with PC1 temperature, total organic carbon, are: oxydability of permanganant of potassium and the hydrogen potential. The temperature, total organic carbon, oxydability are positively to the PC1. The hydrogen potential is negatively correlated to PC1, we observe a very strong correlation between the two indicators of organic matter (TOC and Oxydability). On the axis defind by the PC2, one finds the chlorine which is correlated to this main component. The correlation coefficient of Pearson gives an idea on the interrelations and dependencies existing between the chemical elements. This coefficient is between -1 and 1, indicating a presumption of linkage between the two series as much as it approaches 1 in absolute value [17]. It is found that the THMs are at the center of the factorial plane which means that they have no correlation and the values obtained are not continuous variables. An element close to the center is probably better explained by other main component other thane PC1 and PC2. Chlorine and temperature occupy the upper right quarter of the factorial plane, so these factors have positive bonds with PC1 and PC2. TOC and oxydability of permanganate of potassium occupy the lower right quarter of the plane, these two elements therefore have positive links with PC1 and negative with PC2. The pH occupies the lower left quarter of the factorial plane, the pH therefore has a negative bond with PC1 and PC2. The analysis of the distribution of the samples in the factorial planes makes it possible to demonstrate the similarities and dissimilarities existing between the samples and their elementary components.

In order to identify these links between the samples and their chemical composition, the coordinates of the observation in the factor plots PC1 and PC2 have been shown in Fig. 7



Figure 7: Distribution in the factorial plane

In the first group that groups samples from Frantz Fanon and Soumaa their location in this position is related to their values in Hydrogen Potential pH. A second observation is essentially defined by the samples taken at El-Affroun, the location is related to TOC and oxydability of potassium permanganate. A third group includes the samples form the two water towers of Chiffa and Mouzaia, their common point being related to the values of temperature of the water and those of chlorine.

CONCLUSION

The data collected in this study allowed us to determine the physicochemical quality influencing the formation of Trihalomethanes in waters of Soumaa, Frantz Fanon, El-Affroun, Mouzaia and Chiffa (Blida-Algeria). result showed that the The water temperature of the town Soumaa and El-Affroun is higher compared to the other water towers. This increase is explained by weather and seasonal variation, the pH of the water is very close to neutrality, the concentration of the two indicators of organic matter are relatively low in the five water towers. Chlorine levels ranged from 0 to 0.7 mg/l.

The Trihalomethanes assay used in this study is that of gas chromatography coupled to Headspace and an Electron Capture Detector.

This simple method is effective because of its speed and ability to analyze several samples at the same time and with a limit quantification of $5\mu g/l$. The analytical results of the four **THMs** compounds showed concentrations below $\mu g/l$, which means that the 5 waters studied do not contain THMs.

The statistical study by principal component analysis PCA shows a strong correlation between the two indicators of organic matter.

These results showed clearly that the water distributed in the cities of Soumaa, Blida, El-Affroun, Mouzaia and Chiffa does not contain THM, so there is no health risk associated with THMs.

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