

# Monitoring of Haloacetic Acid Concentration in Swimming Pools by Using GC-MASS Analyzer in Zanjan City-Iran

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## Abstract

Haloacetic acids (HAAS) are the main groups of disinfection by-products that have high health risks. In this investigation, determination of trichloroacetic acid and dichloroacetic acid as two main product of chlorination procedure of water treatment was measured in some swimming pools of Zanjan city-Iran. After sampling, gas chromatography tandem mass spectroscopy method (GC/MS) was used for analyzing of these two chlorinated by-products. Six samples of swimming pools were studied in two summer and winter seasons. The average amount of trichloroacetic acid and dichloroacetic acid concentration was ranged between not detectable (ND) to 6.80  $\mu\text{g L}^{-1}$  and 0.06 to 1.45 in summer, and 0.29–5.13 and 0.27-17.12 in winter. The concentration of these haloacetic acids in tap water sample was lower than swimming pools and observed 0.26  $\mu\text{g L}^{-1}$  and not detectable (ND) for dichloroacetic acid and trichloroacetic acid, respectively.

**Keywords:** Haloacetic acids, Swimming pool, Disinfection by products, Trichloroacetic acid, Dichloroacetic acid.

## Introduction

Disinfection of drinking water has been done to prevent diseases and eliminate microbial agents (Bond et al., 2012). There are manifold methods for disinfection of water, such as chlorination and ozonation, but among these procedures, chlorination is very common. Swimming pools are one of important public places in which people can catch many diseases. Swimming pools are places for exercise, treatment and rest. They can be disinfected to provide proper sanitation by chlorination methods otherwise; they can carriers of germs and infectious diseases (Espino et al., 2013; Cardador& Galleg, 2011).

In swimming pools that treated with chlorination, due to inter organic compounds from swimmers' body they contain more natural organic matter (OM) than drinking waters. Combination of chlorine with organic matters in water may cause generation of disinfectant by-products (DBPs)(Simard et al.,2013) For the best asepsis in swimming pools nearly 1-3  $\text{mg L}^{-1}$  chlorine relict are recommended (Wang et al., 2014). Haloacetic acids (HAAs) and trihalomethan (THMs) are two major groups of DBPs that have detrimental result, carcinogenicity, and genotoxicity, for human (Fantuzzi, et al., 2001; Florentin et al., 2011). Dichloroacetic acid has carcinogen effect on humans (Hamidin, 2009). Nonetheless, trichloroacetic acid shows genotoxicity, cytotoxicity in animals' studies around this problem and it is not yet found its carcinogen impact on human beings (Plewa et al., 2010). Natural organic materials are major constituent of total organic compound (TOC) concentration in waters, and they have fundamental role in formation of haloacetic acids and halomethans (Liang et al., 2003).

According to US Environmental Protection Agency the maximum value for concentration of 5 main haloacetic acid containing monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monoboromoacetic acid and diboromoacetic acid in drinking water is

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60 µg L<sup>-1</sup> (Nikolaou et al., 2002).

Furthermore, based on world health organization (WHO) standard concentration for dichloroacetic acid and trichloroacetic acid was mentioned 50 and 200 µg L<sup>-1</sup>, respectively (Lagbas et al., 2016). These values regularly changed in term of swimming pools.

There was different investigation through monitoring of haloacetic acids in drinking water and swimming pools worldwide. Gas chromatography (with electron captured detection (GC-ECD) is one of the methods normally used for detection of haloacetic acids in waters (Wang et al., 2017). Gas chromatography tandem mass spectroscopy (GC-MS) method has been developed because of low limit detection in comparison with electron captured detector and it can detect very low concentration of haloacetic acids. (Yuffeng et al., 2001; Al-Shatri et al., 2014; Xie, 2001). In this study the presence of trichloroacetic acid and dichloroacetic acid in some indoor pools and tap water in two different seasons was investigated. The water sampling was done in Zanjan city –Iran. The method that used for analyzing of samples was GC-MS.

## Materials and Methods

### *Reagents*

Methyl tertiary-butyl ether (98%) as a solvent for extraction and all used chemicals was with analytical grade purchased from Merck Company and used without any purification or pretreatment. Methanol (99%) and sulfuric acid (98%), sodium sulphate (98%), sodium bicarbonate 6H<sub>2</sub>O (98%), copper sulphate (99%) was used in the sample preparation. Trichloroacetic acid (>98%) and dichloroacetic acid (98%) was used for standard preparation.

### *Sample collection*

Water samples were gathered from swimming pools by using glass bottles. Glassware and vessels were treated in 10% (v/v) nitric acid solution for 24 h and were washed with distilled and deionized water. The bottles carried into laboratory within 1 hour and were filtered through 0.45 µm filters. In laboratory in first step, chemical and physical properties measured immediately. Then they stored immediately at 4°C at the refrigerator until used for GC-MS determination.

### *Instruments*

Gas chromatography tandem mass spectroscopy (Varian-Saturn-CP3800 model) was used for determination of dichloroacetic acid and trichloroacetic acid in water. The column used was VF5-MS (5% phenyl) with dimensions 30m ×0.32mm outer layer thickness×0.25 µm film thickness. Injection was made in splitless mode, with helium as carrier gas. Column flow was 1 ml min<sup>-1</sup> and the pressure was 10 psi. The oven temperature program was held isothermally at 40 °C for 2 minutes at a rate of 10 °C min<sup>-1</sup> and then ramped into 280 °C and 10 min hold at this temperature. The electron energy was 70 eV.

The pH, electrical conductivity (EC) and dissolved oxygen (DO) of the samples were immediately measured at sampling stations by using a portable digital pH meter (Hach HQ 40d). Chloride ion (Cl<sup>-</sup> method 8113- Hach) and organic constituent parameter (OC-method 410- Hach) was measured by using DR5000 Hach spectrophotometer.

### *Preparation of standards and calibration curve*

Due to sample matrix contribute to analytical signals, for analyzing of HAAs standard addition method was used. 1 ml extracted pool water and 1 ml each standards of trichloroacetic and dichloroacetic acid were prepared. A 0.1 µg ml<sup>-1</sup> trichloroacetic acid stock standard was prepared by adding 0.01mg accurately weighing of trichloroacetic acid into a 100 ml volumetric flask and diluted with ultra-pure water. The stock standard was diluted to prepare working standards with concentrations of 10, 50, 500, 3000 µg L<sup>-1</sup> for the calibration curve. The stock standard solution of dichloroacetic acid was prepared by adding 3.131 ml of dichloroacetic acid into 50 ml stock solution and then 0.33, 2 and 5 µg L<sup>-1</sup> concentration was prepared. The calibration curve confirms ability of method in determination of trichloroacetic acid and dichloroacetic acid (Fig. 1). The limit of detection (LOD) for this method was defined as the concentration at which signal- to –noise ratio was 3:1.

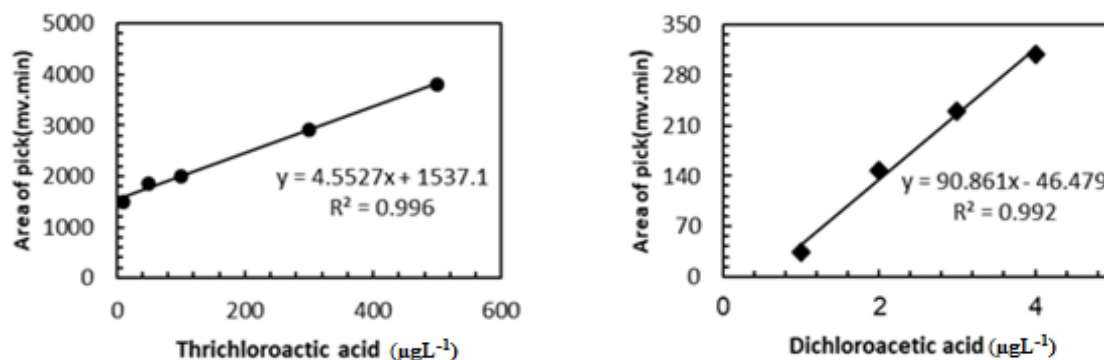


Fig. 1. Calibration curve for dichloro and thrichloroacetic acid

#### Sample preparation and analyzing

EPA-522-2 method was used for analyzing of haloacetic amount with GC-MASS analyzer. In this method 40 ml of sample is adjusted to pH <0.5 and extracted with 4 ml of methyl-tert-butyl-ether (MTBE). The haloacetic acids that have been partitioned into the organic phase are then converted to their methyl esters by the addition of acidic methanol followed by slight heating. The acidic extract is neutralized by a back extraction with a saturated solution of sodium bicarbonate and the target analysts are identified and measured by capillary column gas chromatography using a mass detector (GC/MASS). For this after removing the samples from storage and allowing them to equilibrate to room temperature, 40 mL of the water sample place into a 60 mL glass vial with a Teflon-lined screw cap and the sample pH is adjusted to less than 0.5 by adding at least 2 mL of concentrated sulfuric acid. After shaking, quickly add approximately 2 g of copper (II) sulfate pentahydrate and shacked until dissolved. Blue color of the aqueous phase allows better distinguish between the aqueous phase and the organic phase. Then add 16 g of muffled sodium sulfate to increase the ionic strength of the aqueous phase and shake for three to five minutes until almost all is dissolved. After this process we added 4.0 mL MTBE and place on the mechanical shaker for 30 minutes. Approximately five minutes allowed that the phases were separated. Using a Pasteur pipet, transferred approximately 3 mL of the upper MTBE layer to a 15 mL graduated conical centrifuge tube. Next, 1 mL 10% sulfuric acid in methanol to each centrifuge tube was used. Cap the centrifuge tubes and place in the heating bath at 50°C and maintained for two hours. The vials must fit snugly into the heating block to ensure proper heat transfer. At this stage, methylation of the method analytes is attained. By adding 4 mL saturated sodium bicarbonate solution to each centrifuge tube in 1 mL for neutralization extracted sample. Then exactly 1.0 mL of the upper MTBE layer was transferred to an autosampler vial and in this stage the extracts were ready for analyze.

Figure 3 shows GC/MASS chromatogram for dichloroacetic acid (5.147 min.) and thrichchloroacetic acid (7.758 min.) as an example.

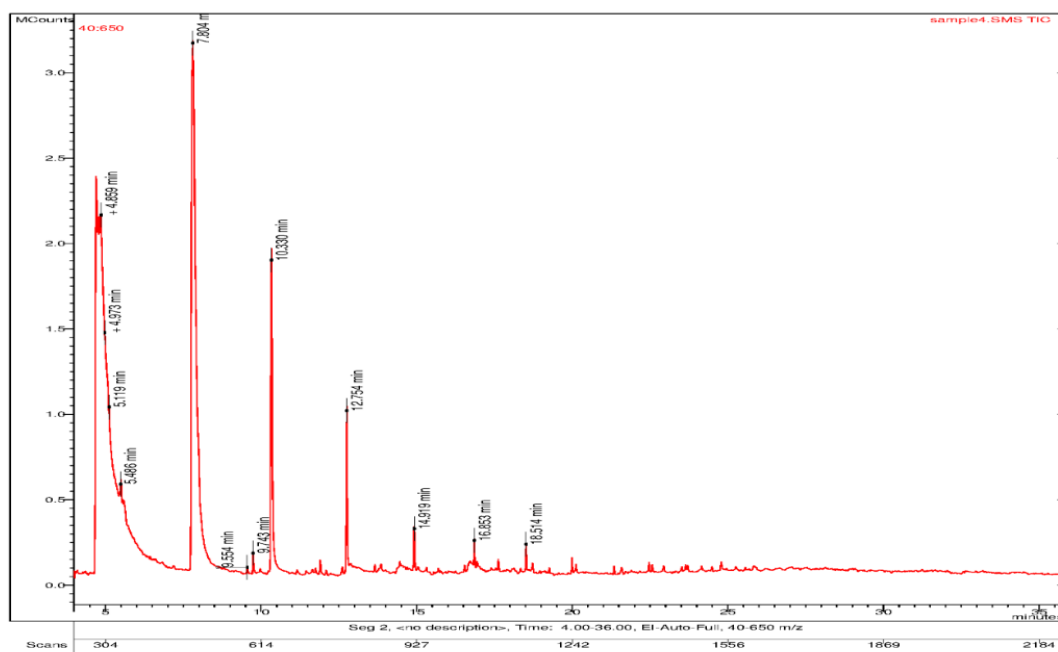


Fig. 2. GC chromatogram of dichloro and thrichloroacetic acid

## Results and Discussion

The results of analysis of water samples from 6 swimming samples in two seasons and two samples water from drinking water treatment site and Taham reservoir dam of Zanjan city are given in Tables 1 and 2. Recorded pH, Cl<sup>-</sup> (mg L<sup>-1</sup>), EC (μs cm<sup>-1</sup>), DO (mg L<sup>-1</sup>), UV-254 (cm<sup>-1</sup>) and temperature (°C) of samples varied in the range of 6.37-7.24, 0.22-8.98, 340-1507, 5.58 -6.93, 0.78-0.97 and 22.4 -26.7 for the summer swimming samples; 6.00 -7.00, 0.21-9.12, 650-1100, 5.20 -6.60, 0.82 -0.96 and 24.0-27.0 for the winter swimming samples, respectively. Also the results show that both dichloro and trichloroacetic acid are detected in 92 % of the samples. The concentration of dichloro and trichloroacetic acid (in μg l<sup>-1</sup>) were found in the range of 0.06 -1.45 and ND (not detectable) -6.80 for the summer swimming samples; 0.27 -17.12 and 0.29-5.13 for the winter swimming samples, respectively.

As shown in table 2 in winter the swimming pools water were warmer in comparison with summer due to cold weather outside. The same is true for chloride ion. This caused accelerating total organic compounds level in pools and consequently the concentration of summation DCAA and TCAA increased by accumulating of TOC and combination of chlorine ion with DBPs. On the other hand, It may be said that with increasing temperature the concentration of haloacetic acids the decreases. It should be noted that HAAs are non-volatile compounds and the heat formation of HAAs was at temperature above 20 °C, and boiling point of these two haloacetic acids were above 50 °C, this phenomenon couldn't reduce the TCAA and DCAA value pool water in the winter (Wang et al., 2014).

Another important result that was confirmed in the table 2 was that the DCAA values were highly amount in winter than TCAA concentration, which this trend has been reversed in the summer. In winter, given that people spend less exercise on swimming pools, the chlorination rate is somewhat lower than in the summer, as a result of this lighter chlorination by products (DCAA) were more visible in swimming pools the winter. It is noteworthy that there is not a report for formation mechanism of trichloroacetic acid form dichloroacetic acid and there is no relation in their concentration (Kou et al., 2004).

The given data for drinking water from drinking water treatment site of Zanjan city show low concentration amount of haloacetic acids in comparison of swimming pool samples. For further study one dam around the city was selected and its haloacetic acid amount was determined. This Dam is main source drinking water treatment site. The result indicated that levels of trichloroacetic acid and dichloroacetic acid detected in our study in sampling time were lower than detection limit.

Table 1- Concentration of dichloro and trichloroacetic acid and studied parameters

S.P number	Season	pH	Cl <sup>-</sup> (mg l <sup>-1</sup> )	EC (μs cm <sup>-1</sup> )	DO (mg l <sup>-1</sup> )	UV-254 (cm <sup>-1</sup> )	Tem. (°C)	TCAA (μg l <sup>-1</sup> )	DCAA (μg l <sup>-1</sup> )
1	summer	6.67	0.23	954	6.03	0.94	22.4	3.56	0.81
	winter	6.00	0.21	900	6.10	0.90	25.0	5.13	0.27
2	summer	7.02	1.12	1162	5.58	0.78	26.7	0.55	0.82
	winter	6.20	1.00	1001	5.20	0.96	27	2.49	17.12
3	summer	7.24	8.98	1043	6.17	0.91	23.7	1.37	0.40
	winter	6.65	9.12	980	6.40	0.95	24.5	1.77	9.42
4	summer	6.37	1.12	394	5.98	0.91	23.7	ND	1.45
	winter	7.00	2.30	650	5.70	0.89	26.5	0.29	1.64
5	summer	6.48	0.22	1507	5.98	0.94	23.5	6.80	0.06
	winter	6.10	1.50	1100	6.60	0.91	25.4	2.24	1.77
6	summer	6.54	0.80	340	6.93	0.97	22.5	1.64	1.06
	winter	6.50	1.25	1050	6.54	0.82	24	2.38	0.38
DW	summer	7.00	0.10	450	7.00	0.95	23	0.26	ND
Taham R.	summer	7.80	0.05	1700	7.80	0.99	17.00	ND	ND

S.P number: S.P number UV-254: OC (organic constituent); TCAA: trichloroacetic acid; DCAA: dichloro acetic acid; DW: sample water from drinking water treatment; Taham R.: Taham reservoir dam; ND: not detectable

Table 2- Statistical descriptions of dichloro and trichloroacetic acid and studied parameters

	Season	pH	Cl <sup>-</sup> (mg L <sup>-1</sup> )	EC (μs cm <sup>-1</sup> )	DO (mg L <sup>-1</sup> )	UV-254 (cm <sup>-1</sup> )	Tem. (°C)	TCAA (μg L <sup>-1</sup> )	DCAA (μg L <sup>-1</sup> )
Average	summer	6.72	2.08	900	6.11	0.91	23.75	2.78	0.77
	winter	6.41	2.56	947	6.09	0.90	25.4	2.38	5.10
Minimum	summer	6.37	0.22	340	5.58	0.78	22.40	0.55	0.06
	winter	6.00	2.56	650	5.20	0.82	24.00	0.29	0.27

Maximum	summer	7.24	8.98	1507	6.60	0.97	26.70	6.80	1.45
	winter	7.00	9.12	1100	6.93	0.96	27.00	5.13	17.12
Standard Deviation	summer	0.31	3.11	414	0.41	0.06	1.42	2.24	0.44
	winter	0.35	3.00	146	0.50	0.04	1.06	1.43	6.22
WHO limits (Saba and Tekpor 2015)		7.2-7.8	<3	-	-	-	21-32	200	50

S.P number: S.P number UV-254; OC (organic constituent); TCAA: trichloroacetic acid; DCAA: dichloro acetic acid; DW: sample water from drinking water treatment; MCL: maximum contaminant levels

This was reported that pH, organic constituent (natural organic matter), temperature, total organic carbon (TOC), electrical conductivity (EC), and chloride ion that effected mutability concentration of DBPs (Judd and Bullock, 2003; Pourmoghaddas & Stevens, 2002; Ye et al., 2009). Spearman method was applied for investigation bivariate correlations among the studied parameters. Close relationship between the couples pH/trichloroacetic acid (Correlation coefficient = -0.71; p= 0.01) and chloride ion / trichloroacetic acid (Correlation coefficient = -0.70; p= 0.01) is confirmed. This should be noted that same as a reported paper (Rodriguez et al., 2004). It is proved that there is no relationship between DCAA formation and pH parameter. In acidic water samples TCAA can be formed according to oxidizing property of alkyl groups on the organic compounds (Liang et al., 2003). The swimming pools were below standard sets with regard to pH. The dichloro and trichloroacetic acid as patterns for haloacetic acids were in the standards ranges.

## Conclusion

In summary, the result of this research has shown existence thrichloroacetic acid and dichloroacetic acid in swimming pools of Zanjan city. These amounts were normal level in comparison to WHO standard. This study has also highlighted the need for further research and regular monitoring, in order to determine the permitted levels of haloacetic acid in the swimming pool water. Other parameters such as pH and water temperature, EC, chloride ion and UV-254 were measured and only impact pH and chloride ion on thrichloroacetic acid formation are significant. The pH values were acidic and below the announced WHO value range. The total of two thrichloroacetic acid and dichloroacetic acid in winter was higher than summer but in comparison to other study, such as reported city values of China, US, Canada and Italy is very lower (Table 3).

Table 3- Comparison of dichloro and thrichloroacetic acid in the other study

	Present work	Wang et al., 2013	Wang et al., 2013	Tardif et al., 2016	Righi et al., 2014	Kanan et al., 2011
TCAA ( $\mu\text{g l}^{-1}$ )	0.29-6.80	5-195	20-2970	24.1-249.6	1-403	52-1537
DCAA ( $\mu\text{g l}^{-1}$ )	0.06-17.12	6-98	50-2040	27.4-500	1-291	73-1297
Country and city name	Iran-Zanjan	China-Beijing	United states-Pennsylvania	Canada-Quebec	Italy-Modena	United States

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