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Identification and Quantification of Chloroacetic Acid Derivatives in Tehran Drinking Water: The Role of Effective Factors in Chlorination Process

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In chlorination process for water disinfection, besides on inactivation pathogens, chlorine reacts with natural organic compounds that present in water and lead to the formation of chlorinated byproducts such as chloroacetic acids. In this research, effective factors in formation of compounds of halo acetic acids *via* propanone chlorination reaction were studied. The studied factors were concentration of organic compounds, chlorine dose and pH of sample. The tests results showed that these factors significantly affect on type and amount of chloroacetic acids. The increasing of propanone's concentration and chlorine dose cause an increase in all three types of compounds of halo acetic acids. While, decreasing of pH, leads to increasing of chloroacetic acid concentrations. Identification and determination of halo acetic acids performed with GC instrument and electron capture detector (ECD). The inherent advantages of GC-ECD were highly selective and good resolution toward halo acetic acids, so that the method was ideally suited for trace determination of chloroacetic acids in the investigated urban water samples. In order to evaluation of effective factors on formation of halo acetic acids, resulted from chlorination of organic compounds in urban water resources, several samples were monitored for parameters such as temperature, free residual chlorine, total organic halo acetic acids and pH of Karaj river, chlorinated water from Bilaghan lake, inlet and outlet of Jalalieh water treatment plant.

Key Words: Chloroacetic acids, Natural organic compounds, Gas chromatography, Electron capture detector.

INTRODUCTION

Many water resources, especially surface waters, they contain natural organic compounds which lead to the production of unpleasant odor and taste, reaction products with chlorine and the production of byproducts in drinking water treatment process[1]. The purpose of water purification involves the removal of pathogens and affecting pollutants on qualitative characteristics and water's public acceptance. Water disinfection, is the final stage of the water treatment process. Today, chlorination is the world's most common method of disinfection[2-4]. The most important reasons for the use of chlorine as a disinfectant are; effective at low concentrations, low cost and its availability. In the process of water disinfection, in addition to kill or disable pathogens, natural organic compounds in the water, react with disinfectants and unwanted disinfectant byproducts produced. The main byproducts of chlorinated water are chloromethanes (4 compounds) and haloacetic acids (5 compounds)[5].

Haloacetic acids are carboxylic acids derivatives in which the halogen atoms, are replaced by hydrogen atoms of methyl groups (α-position). These compounds have three separate groups (mono halo acetic acids, di halo acetic and tri halo acetic acids) and they are nine compounds[6].

The united state's environmental protection agency, introduced 5 compounds of halo acetic acids, including mono chloroacetic acid, dichloroacetic acid, trichloroacetic acid, mono bromoacetic acid and dibromoacetic acid as primary pollutants. These compounds are colourless, low volatile, soluble in water and relatively stable. The main source of these compound's production in the environment, is where produce some special medicines (such as topical contractors, anti-fungal, modulation of blood acid, blood sugar and blood fat) and chemicals such as bleach wood pulp for paper production are used[7-10].

Epidemiological studies in 1992 in the united state about potential of chlorinated waters health risk show that 9 % of bladder cancers and 15 % of intestinal cancers of total 10000 cases of cancers in a year caused by chlorination byproducts. Based on categorization of EPA in 1986, dichloroacetic acid is in group B2, is a possibility to cause cancer in human. This possibility is based on efficient evidences on animals and no efficient ones in human kind[4]. Trichloroacetic acid is

categorized in group C. This compound may cause cancer in human. The evidence in animals is limited and there is not enough information about human to assess the carcinogen potential. US. EPA, presents several rules to monitor chloroacetic acids due to danger potential of them on human health[11- 14].

Studies on mouses show that long time contacts with di and trichloroacetic acids that is in the drinking water, causes liver cancer. Halo acetic acids enter to human body *via* food (vegetables, grains, cereals and chlorinated drinking water) and their absorption in the body is *via* blood circle[15]. The higher concentrations than permitted limits have bad effects on liver, kidney, eyes, nervous system[7,8]. These compounds are not absorbable by skin.

Hence, because of concerns about risks of these compounds on human health, investigation of effective factors on chloro acetic acids formation during the chlorination process and determination of this group of compound's amounts in drinking water is necessary.

Tehran city's drinking water provides *via* surface and ground waters. Surface waters include Karaj River, Jajrood river and Laar river,Water of Karaj river, after transferring to Amir Kabir dam, transfers again to Bilaghan basin and consequently after pre-treatment and pre-chlorination, a part of it transfer by steel pipes to Jalalieh water treatment plant.

In this study, effective qualitative parameters on formation of chloroacetic acids (such as the amount of organics, amounts of chlorine injection and injection point of chlorine, temperature and pH) during the treatment process in Jalalieh plant were assessed. Also the amounts of these components in Tehran's drinking water, determined and the results compared with Iranian national standard (1053), world health organization and the United States Environmental Protection Agency's guidelines.

EXPERIMENTAL

In this research, several samples were prepared in a period between November 2010 and June 2011. The samples were of Karaj river (the rare water introduced to Bilaghan basin), chlorinated water in Bilaghan basin outlet, rare water inlet to Jalalieh plant and treated water in plant outlet. To assess the efficiency of treatment process, in mentioned treatment plants, the sampling points selected before coagulation unit and after final chlorination (post-chlorination). According to standard methods, some effective factors in formation of halo acetic acids such as temperature, pH and residual chlorine, were tested in sampling place. Also to sampling and transferring the samples suitable bottles were used. The samples were kept in an ice flask and stored in 4 ºC before transferring to laboratory.

All samples were prepared and analyzed in less than 48 h after sampling. The extraction technique was liquid-liquid extraction and was performed by tertiary butyl ether. Derivation of samples (esterification) performed by a mixture of sulfuric acid-methanol 10 %. To qualitative and quantitative determinations of three chloroacid compounds, a gas chromatograph equipped with a 30 m capillary column and electron capture detector[14].

In this study, 2-bromobutyric acid was used as internal standard because of its properties and suitable retention time. To plot a calibration curve, a standard mixture solution of three chloroacetic acids (mono di and trichloroacetic acid) in definite concentration prepared. The standard solutions after preparing and extraction (exactly like analyte samples) introduced to GC/ECD. For each standard solution, all stages repeated 3 times and each point of calibration curve resulted of average of three successive measurements. The calibration curve for each analyte plotted based on the ratio of analyte peak area to internal standard peak area. Detection limit and quantitative determination limit for each analyte determined based on signal to noise ratio 3:1 and 10:1 respectively with coefficients of variables less than 20. The accuracy of method resulted based on its reproducibility on three consecutive analyses. The accuracy in all determined samples was less than 5% that indicates reliability of the developed method. To determination of organics in samples the method number 5319 of standard methods was used[7].

RESULTS AND DISCUSSION

Effect of organics amount: In the chlorination reaction of propanone, increasing the organic carbon (propanone) causes the increasing of all three kinds of chloroacetic acids (mono, di and trichloroacetic acid). The effect of propanone on formation of three kinds of chloro acetic acid is not same. Addition of organic carbon has the maximum effect on production reaction of dichloroacetic acid and the minimum growth refers to trichloroacetic acid (Fig. 1).

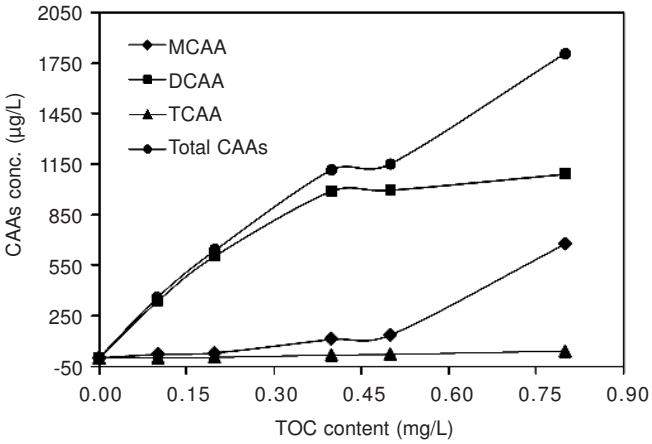

Fig. 1. Effect of TOC on formation of monochloro acetic acid, dichloro acetic acid and trichloro acetic acid and Total chloro acetic acids

Effect of chlorine: In chlorination reaction of propanone, increasing the injected chlorine causes the increasing of all three kinds of chloroacetic acids (mono, di and trichloro acetic acid). The effect of injected chlorine on formation of three kinds of chloro acetic acid is not same. Addition of organic carbon has the maximum effects on production reaction of mono dichloroacetic acid and the minimum growth refers to trichloroacetic acid (Fig. 2).

Effect of pH: In chlorination reaction of propanone, increasing the amount of pH causes the decreasing of all three kinds of chloroacetic acids (mono, di and trichloroacetic acid) The effect of pH amount on formation of three kinds of chloro acetic acid is not same. It has the maximum effects on dichloroacetic acid and the minimum effect refers to trichloro acetic acid (Fig. 3).

TABLE-1
INFORMATION OF INLET AND OUTLET WATER OF BILAGHAN LAKE DURING 8 MONTHS IN 2011-2012

Time period	T (°C)	pH	Cl_2 (mg/L)	TOC (mg/L)	MCAA (µg/L)	DCAA (µg/L)	TCAA (µg/L)	Total CAAs (µg/L)
INLET WATER								
October	13.0	7.91	0.0	0.38	1.21	1.71	0.65	57.3
November	10.2	8.03	0.0	0.45	7.45	0.47	0.05	7.92
December	8.0	7.80	0.0	0.33	0.05	0.62	0.05	0.62
January	6.0	8.10	0.0	0.65	< 0.05	< 0.05	0.12	0.12
February	6.0	8.09	0.0	0.38	< 0.05	< 0.05	< 0.05	< 0.05
March	7.0	7.54	0.0	0.90	< 0.05	< 0.05	< 0.05	< 0.05
April	7.0	7.39	0.0	0.39	0.12	0.13	0.67	0.92
May	8.0	7.12	0.0	0.23	0.77	< 0.05	< 0.05	0.77
OUTLET WATER								
October	13.5	7.49	1.6	0.35	5.35	3.20	0.36	8.91
November	11.2	7.58	1.6	0.41	8.65	0.67	< 0.05	9.32
December	9.0	7.59	1.5	0.29	< 0.05	1.35	< 0.05	1.35
January	6.0	7.87	1.7	0.58	71.95	< 0.05	3.90	75.85
February	6.0	7.87	1.5	0.25	65.4	< 0.05	2.50	67.9
March	7.0	7.03	1.5	0.79	80.74	2.39	0.76	83.86
April	8.0	9.92	1.5	0.22	70.84	1.37	1.75	73.96
May	9.0	7.10	1.0	0.20	8.05	0.05	0.06	8.16

MCAA = Monochloro acetic acid; DCAA = Dichloro acetic acid; TCAA = Trichloro acetic acid; CAAs = Chloro acetic acids.

TABLE-2
INFORMATION OF RAW AND TREATMENT WATER OF JALALIEH PLANT DURING 8 MONTHS IN 2011-2012

Time period	T (°C)	pH	Cl_2 (mg/L)	TOC (mg/L)	MCAA (µg/L)	DCAA (µg/L)	TCAA (µg/L)	Total CAAs (µg/L)
RAW WATER								
October	15.5	7.97	0.5	0.32	5.53	5.40	0.70	11.45
November	14.0	7.03	0.5	0.34	8.78	5.33	0.21	14.45
December	9.0	7.54	0.5	0.22	8.44	3.15	0.16	11.59
January	7.0	7.50	0.6	0.50	115.33	>0.05	0.31	115.66
February	8.0	7.76	0.7	0.20	75.2	>0.05	1.4	76.6
March	8.0	7.60	0.7	0.58	97.01	2.11	0.65	99.77
April	10	7.39	0.6	0.19	75.97	1.83	1.93	79.73
May	12	7.50	0.3	0.18	13.44	0.18	0.11	13.73
TREATMENT WATER								
October	15.0	7.50	0.90	0.28	7.18	8.00	0.54	15.72
November	15.0	7.15	0.70	0.31	11.96	7.76	0.15	20.18
December	10.0	7.23	0.80	0.20	10.19	4.27	0.28	14.74
January	8.0	7.31	0.90	0.46	143.97	0.27	1.00	145.24
February	9.0	7.52	0.80	0.18	83.7	0.1	1.2	85.00
March	9.0	7.48	0.90	0.51	126.41	4.07	1.46	130.94
April	11.0	6.98	0.90	0.17	79.19	1.90	1.94	83.03
May	13.0	6.70	1.0	0.14	20.64	2.82	1.86	25.32

MCAA = Monochloro acetic acid; DCAA = Dichloro acetic acid; TCAA = Trichloro acetic acid; CAAs = Chloro acetic acids.

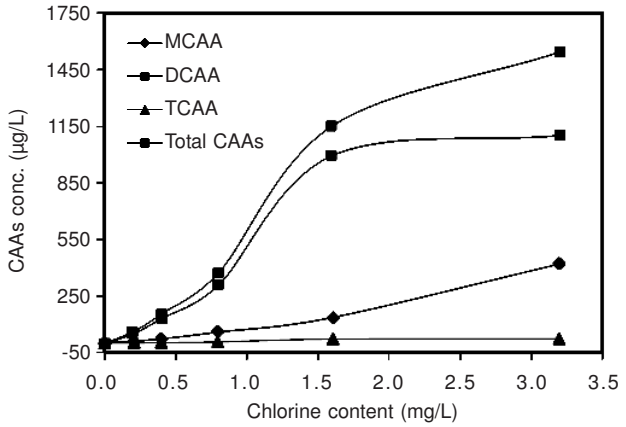

Fig. 2. Effect of chlorine on formation of monochloro acetic acid, dichloro acetic acid and trichloro acetic acid and total chloro acetic acids

The US-EPA because importance of pH effect on coagulation process that leads to removal of organics from water. The obtained results of Karaj river's water samples (inlet water to Bilaghan), chlorinated outlet water of Bilaghan, rare water entered to Jalalieh treatment plant and chlorinated water in Jalale palnt are given in Tables 1 to 2.

The results show presence of natural organics in Karaj river water so that it has more affinity toward compounds of halo acetic acids formation during the pre-chlorination in Bilaghan basin.

The results of identification and determination of compounds of halo acetic acids indicate also that because of high concentration of injected chlorine and presence of organic carbon in Karaj river's water, pre-chlorination significantly causes formation and increasing the compounds of halo acetic acids.

During the chlorinated samples transferring from bilaghan basin to Jalalieh plant, there is enough time for chlorine to react with compounds of halo acetic acids and increase their concentration (Fig. 3).

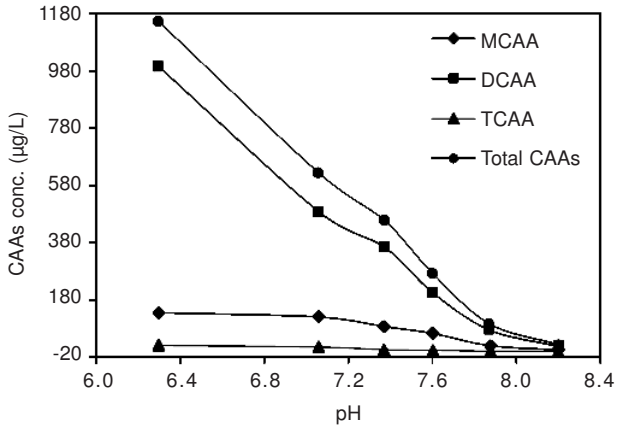

Fig. 3. Effect of pH on formation of monochloro acetic acid, dichloro acetic acid and trichloro acetic acid, Total chloro acetic acids

In comparison with outlet water from Bilaghan basin, residual chlorine and also amounts of organics, in inlet water of Jalalieh plant were decreased but in a same time, the compounds of halo acetic acids amounts showed an increase. It is because of chlorine reaction with organics during the transferring time from basin to plant.

Analyzing the results indicate that the chlorinated outlet water from Jalalieh plant has less organics and more compounds of halo acetic acids for treated water in compare with Bilaghan basin.

In World Health Organization guidelines and Iranian national standard (no 1053) the permitted limits for dichloroacetic acids and trichloroacetic acids are 50 and 200 µg/L respectively. The test results show that for both di and trichloro, they are less than those permitted limits.

Conclusion

The results of propanone chlorination reaction show that increasing in propanone and chlorine concentration leads to an increase in all 3 kinds of compounds of halo acetic acids specially dichloro acetic acid. While, increasing of pH leads to decreasing of formation potential of halo acetic acids because of hydrolyze condition. The results of analyte samples show that Karaj river water has a potential to produce compounds of halo acetic acids due to containing natural organics. And when the water transfer from Bilaghan to Jalalihe plant, there is enough time to occur a reaction between organics and injected chlorine and the result is formation of compounds of halo acetic acids and increasing their concentration in water. The process of TOC'S concentration decreasing and increasing in chloro acetic acid'S concentration in Bilaghan's inlet water, pre-chlorinated water in Bilaghan basin's outlet, Jalalieh plant's inlet water and Jalalieh plant's treated (and chlorinated) water in 8 months (years 2010 & 2011).

Beside on water qualitative parameters such as pH, residual amounts of chloro compounds, the water treatment processes significantly affects on chloro acetic acid's formation, removal and type of byproducts in drinking water. So by optimizing the water treatments processes, formation of byproducts will be controlled with a better efficiency. The following aspects may help to modify the qualitative controls and avoid formation of compounds of halo acetic acids. Omitting the pre-chlorination and replacing the pre-oxidation process with different oxidants such as ozone, chlorine dioxide and multi disinfectors.

Changing the chlorination place was also performed from before coagulation process to after it. Using the biological carbon active to remove the chloro acetic acid's in water supply systems was recommended as a result from this research.

REFERENCES

1. W.E. Coleman, *Environ. Sci. Technol.*, **14**, 576 (1950).
2. G.G. Hawley, The condensed chemical dictionary, New York, NY, Van Nostrand Reinhold, edn 10, p. 241 (1991).
3. R.M. Hozalski, I. Zhang and W.A. Arnold, *Environ. Sci. Technol.*, **35**, 2285 (2001).
4. IARC 2002, Some Drinking Water Disinfectants and Contaminants. Monographs on the Evaluation of Carcinogenic Risks to Humans, p. 84 (2002).
5. D.A. Reckhow and P.C. Singer, *J. Am. Water Works Assoc.*, **82**, 173 (1990).
6. Standard Method for the Examination of Water and Wastewater, edn. 20 (1998).
7. P.W. Stacpoole, *Environ. Health Perspec.*, **106**, 989 (1998).
8. P.W. Stacpoole, *Arch. Disease in Childhood*, **77**, 535 (1998).
9. United States Environmental Protection Agency (USEPA), National Primary Drinking Water Regulation; Disinfectants and Disinfection by Products, Final Rule, Federal Register (1998).
10. United States Environmental Protection Agency (USEPA), Edition of the Drinking Water Standards and Health Advisories (2004).
11. United States Environmental Protection Agency (USEPA), Information collection rule, Washington DC. www.epa.gov/enviro/html/icr/index.html (2008).
12. United States Environmental Protection Agency (USEPA), National Primary Drinking Water Regulations Disinfectants and Disinfection by Products, Final Rule, Federal Register, vol. 63, p. 241 (2012).
13. United States Environmental Protection Agency (USEPA), Method 552/2. Determination of Halo Acetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection (2010).
14. H. Zhou and Y.F. Xie, *J. Am. Water Works Assoc.*, **94**, 194 (2002).
15. S. Reimann, K. Grob and H. Frank, *Mitt. Gebiete. Lebensm. Hygiene*, **87**, 212 (1996).