DETERMINATION OF HALOACETIC ACID IN DRINKING WATER IN CROATIA

Određivanje halooctenih kiselina u vodi za piće u Hrvatskoj

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Introduction:

The most commonly used disinfectants for the treatment of drinking waters are chlorine and its compounds, and the reasons for that are: lower costs, protection against microbial recontamination and minimum level of chlorine residual throughout the distribution system due to high oxidizing potential. [1] Because of its activity, chlorine can also react with natural organic matter (NOM) present in water and form disinfection byproducts (DBP). [2] Studies described approximately 600-700 DBPs which are formed by the common disinfectants. Trihalomethanes (THMs) and haloacetic acids (HAAs) make up more than 80% of the total number. [3] Long-time exposure to high levels of DBPs has been associated with an increased risk of bladder cancer among men. [4] US Environmental Agency has established maximum contaminant level for total trihalomethanes (TTHM) at 80 µg/L and for sum of five HAAs at 60 µg/L. [5] However there is no limit for HAAs in Croatia, only for TTHM which is 100 µg/L. [6] Thus, the aim of this work was to measure HAA levels in tap waters in different parts of Croatia. In addition, total organic carbon (TOC), total trihalomethanes (TTHM) and consumption of $KMnO_4$ was determined in order to study their correlations with HAA.

Materials and methods:

Samples covered different water types and qualites. All disinfection of water tretment involves the use of chlorine. The sampling period was over a one month in the winter of 2019. Prior to sampling ammonium chloride was added to the Winkler glass bottles to convert free chorine residual in the sample matrix to combined chlorine. Tap was opened and the system was allowed to flush and samples were collected from the flowing system. Samples were mainteined away from light and at 4°C until extraction. Modified US EPA Method 552.3 was used for the determination of the HAAs. The method uses gas chromatography system coupled with electron capture detector and capillary column. The GC conditions are presented in Table 1. Sample preparation: 30 ml of sample is extracted with 3 ml of methyl tert-butyl ether (MTBE) containing an internal standard (1,2,3-trichloropropane at concentration 300 µg/L). The HAA are extracted to organic phase and converted to their methyl esters with 10% H_2SO_4 in methanol. Samples are heated for 2 hours and after that organic phase is separeted from methanol and neutralized with sodium sulfate. [7]

Table 1. GC system information

GC method	HAA
Intrument	Thermo Scientific "GC Trace 1300"
Injection unit	splitless (0.5 min)
Detector	ECD
Detector temperature/°C	300
Column	Gold TG-1701 MS GC
Gradient	40°C (10 min), 5°C/min, 75°C (5 min), 10°C/min, 150°C (5 min)
Injection temperature/°C	200
Injecion volume/µL	2 µL

Calibration standards ranged from 0.1 to 20 µg/L and were treated the same way as samples. The analysis of five HAA were made: monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA) and dibromoacetic acid (DBAA). Quality assurance was conducted by participation in proficiency testing (PT). TOC measurement were performed on Shimadzu TOC-LCSH FA E200, 3 measurements of each sample were made and results were expressed as mean value. Consumption of $KMnO_4$ was determined with titrimetric method. TTHM concentrations were determined using GC-ECD instrument.

Results:

Individual HAA concentractions are shown in Table 2. Total HAA concentrations ranged from 0.1 – to 17.2 µg/L with maximum HAA concentration found in Daruvar (Figure 1). Figures 2 – 6 shows correlation between THM, HAA, TOC and consumption of $KMnO_4$. Determined correlation factors are presented in Table 3. Among studied HAAs the higest abundance was found for dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA).

Table 2. Individual haloacetic acid levels (µg/L) in Croatia

	Slunj	Rakovica	Ogulin	Senj	Brinje	Otočac	Našice	Donji Miholjac	Novalja	Vir	Pisarovina	Krašić	Čazma	Kapela	Virovitica	Daruvar	Grubišno polje	Sali	Duga Resa	Ozalj	Đurđevac	Pakrac	Nova Gradiška	Blato
MCAA (µg/L)	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	1.4	BLQ	BLQ	BLQ	0.7	BLQ	BLQ	BLQ	BLQ
DCAA (µg/L)	1.9	3.0	3.6	4.0	0.5	3.5	4.0	0.1	5.1	0.7	BLQ	0.5	BLQ	BLQ	0.4	10.0	BLQ	0.4	4.2	0.9	0.9	9.2	4.2	0.3
TCAA (µg/L)	0.8	BLQ	4.0	5.0	1.1	BLQ	3.0	BLQ	11.3	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	5.9	BLQ	BLQ	1.9	0.3	0.3	5.7	7.9	BLQ
MBAA (µg/L)	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	0.5	BLQ	BLQ	BLQ	BLQ	0.9	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ
DBAA (µg/L)	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	0.4	BLQ	6,0	BLQ	BLQ	0.7	BLQ	BLQ	BLQ	BLQ	2.3	BLQ	BLQ	BLQ	BLQ	BLQ	4.2

	Metković	Ploče	Makarska	Imotski	Hrvatska Kostajnica	Hrvatska Dubica	Jasenovac	Petrinja	Glina	Topusko	Gospić	Gračac	Knin	Korenica	Bešišće	Beli Manastir	Darda	Vrbovsko	Delnice	Novi Vinodolski	Ivanec	Susak	Mali Lošinj	Rab
MCAA (µg/L)	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	1.6	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ
DCAA (µg/L)	0.2	0.3	BLQ	0.8	BLQ	0.2	1.1	4.2	BLQ	BLQ	BLQ	0.3	BLQ	BLQ	4.3	BLQ	1.9	3.2	3.2	1.3	0.2	BLQ	BLQ	BLQ
TCAA (µg/L)	BLQ	1.5	BLQ	BLQ	BLQ	BLQ	0.2	1.3	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	3.1	BLQ	2.8	3.5	4.3	BLQ	BLQ	BLQ	BLQ	BLQ
MBAA (µg/L)	0.3	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ
DBAA (µg/L)	5.7	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ

BLQ-below limit of quantification

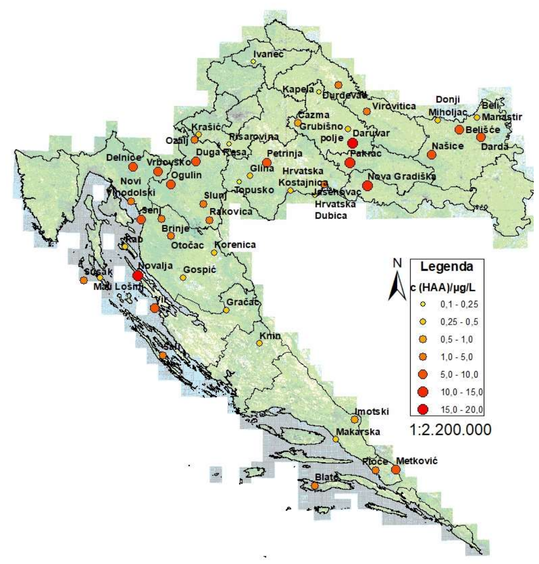

Figure 1. Total haloacetic acid concentration on map of Croatia.

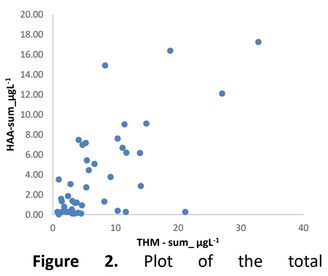

Figure 2. Plot of the total trihalomethane levels versus total haloacetic acid levels in Croatia.

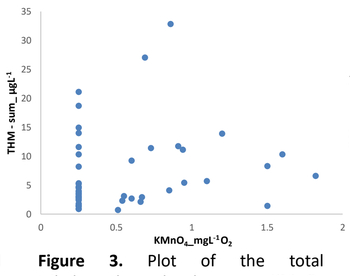

Figure 3. Plot of the total trihalomethane levels versus $KMnO_4$ levels in Croatia.

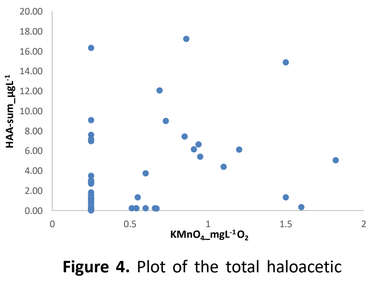

Figure 4. Plot of the total haloacetic acid levels versus $KMnO_4$ levels in Croatia.

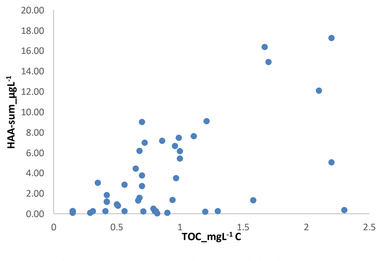

Figure 5. Plot of the total haloacetic acid levels versus total organic carbon levels in Croatia.

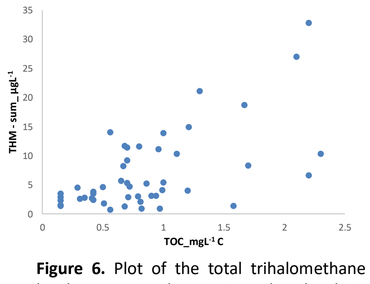

Figure 6. Plot of the total trihalomethane levels versus total oraganic carbon levels in Croatia.

Table 3. Correlation coefficinets

	$KMnO_4$	TOC	HAA
THM	0.03	0.4	0.5
HAA	0.1	0.4	/

Conclusion:

Results show that HAA levels in tested Croatian drinking water are under US EPA maximum contaminant level of 60 µg/L. There is correlation between THM versus HAA concentration, and between THM/HAA concentration versus TOC concentration. The correlation between THM/HAA concentration and consumption of $KMnO_4$ is very poor and could be related to the lower method sensitivity. This is the first published study that has measured HAA levels in Croatia and it provides intresting information of HAA levels, however this study is based on relatively few samples during one sampling campaign and further work is required.

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Literature:
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