

SUBSTANTIATION OF HALOGENATED BY-PRODUCTS GENERATION IN THE CHLORINATION PROCESS OF NATURAL DRINKING WATER RESOURCES BY ANALYTICAL INVESTIGATION

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Abstract

Chlorine, the most commonly used disinfectant for drinking water treatment industry, has also application for several other water treatment objectives, such as: oxidation of iron, manganese, hydrogen sulfide and ammonia, prevention of algal growth in sedimentation basins, maintenance of biological stability of drinking water by prevention of bacteria regrowth in the distribution system.

Natural organic matter (NOM) like humic substances present in water resources reacts with aqueous free chlorine or free bromine, halogenated by-products being formed.

Only a small percentage of halogenated by-products has been regulated in drinking water, most of them with adverse effects on human health: trihalomethanes (THMs) with MAC of 80/100 µg/L (US/EU regulations) and haloacetic acids (HAAs) with MAC of 60 µg/L (only US regulations).

A main indicator of the amount of halogenated by-product that could be expected to form in the distribution system if chlorine is applied in water treatment (oxidation/disinfection steps) is considered to be "disinfection by-products potential formation (DBPF)". For evaluation/quantification of some halogenated by-products (THMs and HAAs) generated by the reactions between chlorine/bromine and NOM, performant analytical investigation methods are needed.

Key words: *surface water, chlorination, trihalomethanes, haloacetic acids*

1. Introduction

The drinking water sources represented by surface water(lakes, rivers including the Danube) are most used in Romania, but also the most exposed to anthropic pollution. For surface water, classic treatment flow, coagulation-flocculation-

settling-filtration-disinfection, is completed with one/two steps of oxidation (pre-oxidation before coagulation-flocculation and post-oxidation, after coagulation-flocculation or filtration) and/or a step of adsorption on activated carbon, depending on the impurification matrix of raw water. The main chemical reagent used in pre-oxidation and disinfection steps is chlorine, which can generate by-products in the presence of natural organic matter (NOM). According to the literature data, only 1% of chlorine used for disinfection turns in halogenated secondary products (TOX) with different volatility degrees.

From the total content of TOX, trihalomethanes (THMs) represent almost 30% [1]. NOM and phenolic compound, anilines and their derivatives, metabolites of algae etc. [2, 3] are classes of compounds with high THM productivity, named THM's precursors.

The generation of halogenated organic compounds TOX and THMs in drinking water treatment plants depend on water resources nature, work conditions and other factors:

- the presence of THM's organic precursors (natural and anthropic organic local);
- use of chlorine and its derivatives in oxidation and disinfection phases;
- excess of chlorine used in disinfection that can cause the THMs generation in storage vessels and in the distribution network;
- the presence of some associated pollutants as bromide ions.

In general, from the total content of THMs, chloroform is the main product (72-93%) of chlorination, in the absence of bromide ions. According to literature study, the high reactivity of humic acids in front of chlorine is due to polyhydroxy benzene units from their structure (n- and p- dihydroxy aromatic compounds). It is estimated that 1 mg/L of humic acid can generate 25 ± 4 $\mu\text{g/L}$ chloroform.

Besides THMs, other chlorinated derivatives with toxic potential are the class of haloacetic acids (HAAs).

2. Experimental part

The aim of the experimental tests was to evaluate the reactivity of natural organic matter (NOM) existing into surface water matrix (Danube water samples D1, D2) towards chlorine used in water treatment, by determination of DBPF (THMs and HAAs) in specific conditions from decanted raw water. The main research activities were as follows:

- evaluation of physical-chemical characteristics of raw water from Danube river, Bechet area, samples D1, D2 (2016);
- elaboration of a new method for evaluation of haloacetic acids (HAAs) containing chlorine and bromine, using GC-ITMS;

- experimental tests for evaluation of THMs and HAAs concentration level in treated water with chlorine (Cl_2 doses ≤ 50 mg/L), after 2 to 6 contact days.

Raw water physical-chemical characterization

For Danube (Bechet area) water characterization, sampling and preservation of water samples were performed using standard techniques. All the analytical investigations were performed according to standardized methods. Main physical-chemical characteristics of studied raw waters are presented in Table 1. Analytical investigations performed in 2016 (two sampling campaigns in June) conducted to the identification of pollutants situated over the admitted limits (MAC): total suspended matter (TSS), PAHs, TNK.

Table 1 Physicochemical characterization of raw water from Danube, Bechet area

	Indicator	MU	D1	D2	MAC
1	pH	-	7.9	7.6	6.5-8.5/5.5-9
2	Turbidity	NTU	205	32.6	-
3	COD _{Cr}	mgO ₂ /L	<30(24.6)	<30(10)	10/20/30
4	COD _{Mn}	mgO ₂ /L	12.2	6.1	-
5	TSS	mg/L	313	63	25/-/-
6	Total hardness	°d	9.5	9.8	-
7	Phenols	mg/L	<0.02	<0.02	0.001-0.1
8	Anionic detergents	mg/L	<0.1	<0.1	0.2-0.5
9	Petroleum ether extractable matter	mg/L	<20(0.2)	<20(0.2)	0.005-0.5
10	NH ₄ ⁺	mg/L	<0.1	<0.1	0.05/1.5/2
11	TKN	mg/L	1.8	1.6	1/2/3
12	Organophosphorus pesticides	µg/L	<0.003	<0.003	0.66
13	Organochlorine pesticides	µg/L	0.075	<0.001	0.77
14	Triazine pesticides	µg/L	<0.008	<0.008	1.37
15	PAHs	µg/L	2.5	0.0087	0.2/0.2/1

Elaboration of GC-ITMS methods for studied DBP

This study focus on chlorine and/or bromine THMs (four compounds) and HAAs (nine compounds), described in Table 2.

For gas chromatographic evaluation of THMs and HAAs concentration an Agilent 7890A gas chromatograph coupled with an Agilent 240 Ion Trap Mass Detector was used. For THMs, head space-GC/MS analysis was used, according to EN ISO 22155, using 10 mL of liquid sample.

For HAAs, liquid-liquid extraction and conversion of HAA to corresponding methyl esters, followed by GC/MS analysis was used, with an modified method, derived from US EPA method 552.2 [4, 5], using 100 mL of liquid sample. For extraction, MTBE was used and for derivatization, methanol: H₂SO₄ with volume ratio 1:9. All nine methylated HHAs were identified using full scan mode, using NIST mass spectra database, and quantified using single ion monitoring mode for characteristic ion for each HAA methyl ester. Calibration curves for concentration values of each HAA between 0.1 and 10 µg/L were obtained with good linearity (r^2 between 0,987 and 0,999).

Table 2 Studied THMs and HAAs

<i>Class</i>	<i>Compound</i>	<i>Abbreviation</i>	<i>CAS number</i>
THMs	trichloromethane	CHCl ₃	67-66-3
	bromodichloromethane	CHBrCl ₂	75-27-4
	dibromochloromethane	CHBr ₂ Cl	124-48-1
	tribromomethane	CHBr ₃	75-25-2
HAAs	monochloroacetic acid	MCAA	79-11-8
	monobromoacetic acid	MBAA	79-08-3
	dichloroacetic acid	DCAA	79-43-6
	bromochloroacetic acid	BCAA	5589-96-8
	dibromoacetic acid	DBAA	631-64-1
	trichloroacetic acid	TCAA	76-03-9
	tribromoacetic acid	TBAA	75-96-7
	bromodichloroacetic acid	BDCAA	71133-14-7
chlorodibromoacetic acid	CDBAA	5278-95-5	

Experimental test for DBP (THMs and HAAs) evaluation

The experimental tests for DBP determination were performed using chlorine water (Cl₂=700 mg/L) and raw water after gravitational settling (2h, remanent turbidity <30NTU) in the following conditions: pH= 7-7.5; reaction time/ contact time : 1-6 days; temperature: 20°C; Cl₂ doses: 25 mg/L (samples D1/1, D2/1) and 47 mg/L (samples D1/2, D2/2) (chlorine solution/water = 700 mg/L); MAC/ UE, RO = 100 µg TTHM (total trihalomethanes)/L.

The analytical investigations of THMs concentrations were done after 2, 5 and 6 contact days between raw water samples and chlorine. Obtained results are presented in *Table 3*.

Table 3 Total THMs potential formation

Sample	TTHMs, $\mu\text{g/L}$		
	$\tau_c = 2$ days	$\tau_c = 5$ days	$\tau_c = 6$ days
D1/1	9.2	16.4	19.9
D1/2	15.9	22.4	26
D2/1	4.9	9.3	16.5
D2/2	6.5	10.7	25.2

A different evolution of THMs and HAAs formation was observed in this study, as follow:

- the maximum concentration of THMs, after 6 day contact, was 25 $\mu\text{L/L}$, below $\text{MAC/UE}=100 \mu\text{g/L}$
- the HAAs concentration is two time higher than $\text{MAC/USA}(\text{HAA}_5 = 60 \mu\text{g/L}$, $\text{MCA}+\text{DCA}+\text{TCA}+\text{MBA}+\text{DBA}$), over 99.8% of haloacetic acids being chloroacetic ones ($\text{TCA} > \text{DCA} > \text{MCA}$).

Table 4 HAAs potential formation

D1.2	HAAs, $\mu\text{g/L}$
	$\tau_c = 6$ days
MCA	14.29
MBA	<0.1
DCA	47.81
TCA	52.59
DBA	0.18
BCA	3.22
BDCA	2.21
CDBA	0.15
TBA	<0.1
Total 1-5 (HAA_5)	114.87
Total 1-9 (HAA_9)	120.50

3. Conclusions

- Natural organic matter existing in drinking water resources are able to modify the treated water quality in the presence of chlorine and derivatives, halogenated by-products with adverse effects on human health being formed.

- New methods to identify/evaluate other groups of halogenated by-products must be developed in order to control the level of organic micropollutants in treated water and to take the suitable measures to diminish/avoid their generation.

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