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Validation and application of a GC–MS method for the determination of haloacetic acids in drinking water

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Abstract: Usually, water treatment plants employ chlorine or sodium hypochlorite during the disinfection process, ensuring that there are not any pathogenic microorganisms in water. However, chlorine might react with natural organic matter and lead to formation of potentially carcinogenic by-products regarding human health, such as haloacetic acids (HAAs). Several countries regulate the levels of these acids in drinking water. Therefore, their concentrations must be monitored with the greatest accuracy as possible. In order to achieve this goal, a method through gas chromatography coupled with mass spectrometry (GC–MS) was validated and applied to the determination of HAAs in samples of water destined to the public water service provision from the city of Maringá, Paraná State, Brazil. Measurements between two periods have close recovery values, indicating that the method has good accuracy during the same day. The limits of detection (*LOD*) and quantification (*LOQ*) were satisfactory, with *LOD* 0.42 μg L^{-1} and *LOQ* 1.40 μg L^{-1} for dichloroacetic acid (DCAA) analysis. Recovery values obtained for the nine haloacetics acids (HAA_9) corresponded to 69.9–107.3 % for samples. The repeatability performed for two periods presented close relative standard deviation (*RSD*) values, indicating that the method has good accuracy during the same day.

Keywords: disinfection by-products; gas chromatography; mass spectrometry; merit figures.

INTRODUCTION

The necessity of water treatment for human consumption is very important.[1] For the achievement of a final adequate product, every step during this treatment must be rigorously controlled, since each undesirable compound has its own maximum concentration value. In this context, water treatment plants (WTP)

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have a fundamental role regarding the distribution of high quality water to the population.[2] Several steps are demanded inside a WTP for the preparation of drinking water, such as coagulation, flocculation, sedimentation, filtration, disinfection, fluoridation and pH correction.[3] During water disinfection, several types of compounds could be used, such as chlorine and its derivates, ozone, hydrogen peroxide and potassium permanganate. Chlorine derivates are the most employed for large scale application.[4,5]

The use of disinfectants such as chlorine might lead to the formation of disinfection by-products (DBPs).[6] DBPs are formed when the disinfecting agent reacts with organic matter, especially humic substances, that are naturally present in water to be treated.[7] Among humic substances, humic and fulvic acids are the most relevant compounds regarding DBP formation.[8]

The haloacetic acids (HAAs) are described among the main DBPs. Toxicologic and epidemiologic studies identified that HAAs have carcinogenic, mutagenic or teratogenic activity in the human body, all of them are related with the exposition to several halogenated by-products.[6,9,10] Main DBPs present in chlorine-treated drinking waters are mentioned by important regulations (details are given in Supplementary material to this paper). As HAAs presence is restricted in drinking water, proper monitoring of the concentration of these compounds is necessary.

There are various instrumental techniques for the analysis of HAAs in drinking water, such as capillary electrophoresis, liquid chromatography and gas chromatography (GC). The capillary electrophoresis technique has an extraction step and moreover, the method cannot adequately achieve reliable HAAs detection limits for concentrations in the order of μg L^{-1}.[11] High-performance liquid chromatography requires the use of organic solvents in the elution generating residues of these solvents. One of the main instrumental techniques for separation and analysis of HAAs and most of the volatile DBPs in water samples is GC. Its inherent advantages are: high resolution, detection from nano- to picograms (10^{-9} to 10^{-12} g), fast separation, low cost and ease of coupling to sensitive and selective detectors.[12] Furthermore, it is recognized and recommended worldwide by the main institutions for standardized tests for water analysis, such as Standard Methods for the Examination of Water and Wastewater, Environmental Protection Agency (EPA).[13]

According to Xie,[14] the gas chromatography coupled with mass spectrometry (GC–MS) technique compared to the method of gas chromatography with electron capture detection (GC-ECD), offers advantages, such as increased sensitivity to monochloroacetic acid (MCAA), a cleaner baseline, fewer interfering peaks and short analysis time without compromising the analytical results. Therefore, the objectives of the present article are validation of a method through GC–

–MS and application to the determination of HAAs in samples of water destined for public water service provision in the city of Maringá, Paraná State, Brazil.

EXPERIMENTAL

Details related to sampling, and reagents and standards used, are given in Supplementary material to this paper.

Preparation of standard solutions

Two haloacetic acid methyl ester (HAME) solutions with IS were prepared for use in the procedures of optimization, separation and chromatographic identification. The HAME solutions were prepared by diluting the AccuStandard® solution and the 1,2,3-trichloropropane internal standard (IS) with methyl *tert*-butyl ether (MTBE). One with HAME concentration ranging from 200 to 2000 μg L^{-1} with 200 μg L^{-1} of IS and other with HAME concentration ranging from 40 to 400 μg L^{-1} with 40 μg L^{-1} of IS. These solutions were stored in 2.0 mL autosampler flasks and conditioned in a freezer at –18 °C until analysis.

System for GC–MS analysis

A gas chromatograph (Focus GC, Thermo-Finnigan) coupled to mass spectrometer (DSQ II-Thermo-Finnigan), equipped with a capillary DB-5 column (5 % phenyl – 95 % methylpolysiloxane) of fused silica, 30 m length, 0.25 mm i.d. and 0.25 μm thickness film of stationary phase film (J & W Scientific); mass spectrometer equipped with electron ionization source, quadrupole mass analyzer; data acquisition system through Xcalibur software, which includes the spectral library NIST MS Search version 2.0.

Summary of conditions used for GC–MS analysis

Optimized conditions for the haloacetic acids separation and identification GC–MS system were: for GC, injection volume: 1 μL, carrier gas flow: 1 mL min^{-1}, splitless time: 30 s and injector and transfer line temperatures: 200 and 270 °C, respectively; for MS, ionization source temperature: 200 °C, electron ionization mode at 70 eV and *m*/*z* range in full scan mode: 58–260.

HAA extraction

The extraction method was adapted from the USEPA 552.3 method.[15] In each extraction tube, 20 mL of ultrapure Milli-Q water were added along with 30/50/90 μL of the 2 mg L^{-1} HAAs standard solution (to obtain concentrations of 3, 5 and 9 μg L^{-1} HAA in water) and 20 μL of the 10 mg L^{-1} standard surrogate solution. Approximately 1 mL of concentrated sulfuric acid was added until pH 0.5, and 9 g of granulated anhydrous sodium sulfate to increase the ionic force of the aqueous phase. Then, 2 mL of MTBE with 40 μg L^{-1} of IS were added and the tube was vigorously agitated for 3 min, and after that, the system was allowed to stand for phase separation. With a graduated glass syringe, 1.5 mL of the organic phases was collected for further conversion to their methyl esters.

HAA derivatization

Approximately 1.5 mL of H_2SO_4/CH_3OH in 1/9 volume ratio were added to the tubes containing the obtained HAAs extracts and the system was quickly closed and placed in a heating bath at 50±2 °C for 2 h. After cooling in an ice bath, 4.0 mL of a 1.0 mol L^{-1} sodium sulfate solution were added to the system that was then vortexed for 3 min. The lower layer (aqueous phase) was removed with a Pasteur pipette. Approximately 1.0 mL of saturated sodium bicarbonate solution was added and the tubes were vortexed for 30 s for complete

reaction. The upper phase was collected in an amber autosampler flasks and stored at –18 °C.[15]

Merit figures

Analytical curves. The analytical curves were constructed for the nine haloacetic acids methyl esters (HAAs-me) in the following concentrations: 5, 10, 20, 40, 60, 80 and 100 μg L^{-1} for MCAA-me, DCAA-me, TCAA-me, DBAA-me and TBAA-me; 20, 40, 80, 120, 160, 200 and 400 μg L^{-1} for MBAA-me and BCAA-me; 5, 10, 20, 40, 80, 120 and 200 μg L^{-1} for BDCAA-me; 20, 30, 40, 50, 100, 200 and 300 μg L^{-1} for CDBAA-me; 10, 20, 30, 40, 50, 100 and 200 μg L^{-1} for the surrogate methyl ester. For compound abbreviations, see Supplementary material.

Repeatability. Using standard HAA-me solutions with concentrations of 30, 50 and 90 μg L^{-1}, plus the IS at 40 μg L^{-1}, triplicate injections were performed for these three points on the analytical curve. This procedure was executed twice a day. The method repeatability was evaluated through the relative standard deviation values of the repetitions.

Limit of detection. The recommendations of the EPA 552.3 method[15] were followed for the calculation of the limit of detection (*LOD*). The standard deviation values (*S*) for 9 replicates of a standard HAA-me solution at concentrations between 5 and 50 μg L^{-1} were multiplied by the "test *t*" value of 2.896 for the 99 % confidence level and 8 degrees of freedom: [16]

$$LOD = St_{(n\text{-}1,\ 1\text{-}\alpha\ =\ 0.99)} \quad (1)$$

Limit of quantification. The limit of quantification (*LOQ*) was calculated according to:

$$LOQ = 3.33\ LOD \quad (2)$$

Accuracy (analyte recovery). Samples containing 20 mL of Milli-Q ultrapure water (blank) were fortified with 30/50/90 μL of a 2.0 mg L^{-1} HAAs standard solution. Besides evaluating the recovery percentage of the analytes, the percentage recovery a 10 mg L^{-1} surrogate (2,3-dibromopropanoic acid) standard solution, containing 100 μg L^{-1} in the final extract, was also determined. The analyses were executed in triplicate and the procedure was performed in two periods of the same day (morning and afternoon).

Recovery assay with treated water samples. Three water samples were used for the recovery assay: Z3, Z7 and Esperança (see Supplementary material). Samples were fortified with 30 μL of a 2 mg L^{-1} standard HAAs solution in order to obtain a concentration of 3 μg L^{-1} in the water. The same extraction/derivatization procedure was performed, followed by GC–MS analysis.

Statistical analysis. The data were subjected to ANOVA and the means were compared using the Tukey test conducted using Statistica, version 7.0. Correlation coefficients (R^2) were calculated to determine the relationship between the obtained results using Microsoft Office Excel, version 2007. Principal components analysis (PCA) was realized using MATLAB 2007.

RESULTS AND DISCUSSION

Optimization of the separation and identification of the compounds

To improve the chromatographic separation efficiency, the following variables were tested and optimized: column oven temperature, injector temperature, carrier gas flow, split ratio and time in the splitless injection mode. Details of the chromatographic optimization are given in the Supplementary material to this paper.

The specific *m*/*z* ratio values regarding each analyte monitored in the selected-ion monitoring (SIM) mode are presented in Table I. For method validation and analysis of samples, only the quantification ions (*m*/*z* values with asterisk in Table I) for each compound were monitored in the SIM mode. These quantification ions correspond to an ion with a high *m*/*z* peak in the spectrum that differs from those of other ions present in the adjacent analytes in the chromatogram, in order to increase the signal/noise ratio, eliminate possible interfering signals and increase the sensitivity to the analytes.

TABLE I. Retention times and *m/z* ratio values of HAA-me, IS and surrogate-me fragments which were monitored in the SIM mode; * indicates quantification ions·

Compound	Retention time, min	Fragment mass, *m*/*z*
MCAA-me	6.12	59*, 64, 77
MBAA-me	9.33	59*, 93, 95
DCAA-me	10.07	59*, 83, 85
IS	17.68	61, 75*, 110
TCAA-me	17.92	59, 117*, 119
BCAA-me	18.20	59, 127, 129*
DBAA-me	23.20	59*, 171, 173
BDCAA-me	23.55	59*, 161, 163
Surrogate-me	27.00	59, 165*, 167
CDBAA-me	27.10	59, 207, 209*
TBAA-me	29.25	59*, 251, 253

Merit figures

Method validation was performed based on the following merit figures: the equation and the value of the correlation coefficient (R^2) of the analytical curves, precision (repeatability), limit of detection, limit of quantification and accuracy (recovery of analyte).

Analytical curves. The equations and correlation coefficients (R^2) for the analytical curves of each HAA-me are given in Table II. All analytical curves showed correlation coefficients close to 1, meaning that, within the presented linear range, the prediction behavior of the HAA-me concentrations in relation to the P/IS sign are accurate.

Repeatability. The obtained concentration values were similar to the added concentration values, with exception of CDBAA-me and TBAA-me at 30 μg L^{-1}. The repeatability calculations performed for the mornings presented relative standard deviation (*RSD*) values between 0.41 and 5.73 %, being the smallest for DBAA-me and the largest for CDBAA-me. The results from the afternoon showed *RSD* values between 0.35 and 5.29 %, being the smallest for CDBAA-me and the largest for MCAA-me. The measures between the two periods had similar RSD values (Table III), which indicates that the method has good accuracy during the same day.

TABLE II. Curve equation, correlation coefficient (R^2), limit of detection (*LOD*) and limit of quantification (*LOQ*) for each HAA

HAA	Curve equation	R^2	*LOD* / μg L^{-1}	*LOQ* / μg L^{-1}
MCAA	$y = 0.0077\,x - 0.0081$	0.9998	1.17	3.89
MBAA	$y = 0.0129\,x - 0.0667$	0.9994	0.64	2.13
DCAA	$y = 0.0246\,x - 0.0455$	0.9991	0.42	1.40
TCAA	$y = 0.0109\,x - 0.0226$	0.9988	0.57	1.90
BCAA	$y = 0.0116\,x - 0.0565$	0.9989	0.67	2.23
DBAA	$y = 0.0076\,x - 0.0162$	0.9988	0.43	1.43
BDCAA	$y = 0.0075\,x - 0.0210$	0.9995	0.56	1.86
CDBAA	$y = 0.0015\,x - 0.0063$	0.9994	0.85	2.83
TBAA	$y = 0.0014\,x - 0.0035$	0.9992	0.79	2.63

TABLE III. Mean concentration for each HAA, μg L^{-1}± standard deviation (for analysis in three replicates), in two assays per day

HAA	Assay 1			Assay 2		
	HAA added concentration, μg L^{-1}					
	30	50	90	30	50	90
MCAA	28.7±0.8	47.1±1.0	87.0±0.7	31.0±1.6	51.5±1.0	91.5±1.0
MBAA	31.1±0.9	50.4±1.0	95.5±0.8	30.4±0.6	50.4±0.5	96.4±2.4
DCAA	31.6±1.0	51.6±1.9	90.6±1.3	30.0±1.0	50.0±2.2	95.6±0.7
TCAA	32.0±0.9	50.4±0.8	85.3±2.6	32.3±0.5	52.7±1.7	88.8±2.9
BCAA	30.7±0.9	49.6±1.7	89.2±1.5	31.6±0.4	49.8±0.7	90.4±1.6
DBAA	30.1±0.1	49.8±0.5	88.7±1.0	30.4±0.9	52.7±1.0	92.2±2.4
BDCAA	30.2±1.2	49.4±1.9	90.5±1.8	30.7±0.4	50.1±1.7	90.8±2.8
CDBAA	25.3±1.5	50.0±0.6	91.7±1.9	26.8±0.6	51.0±0.6	89.5±0.3
TBAA	25.7±0.3	48.5±0.8	92.0±0.4	26.5±0.1	49.6±1.5	92.3±0.9

Limits of detection and quantification. The detection and quantification limits are presented in Table II. The obtained values were inferior when compared with those obtained in studies that used other analytical techniques, such as liquid chromatography-electrospray tandem mass spectrometry and gas chromatography coupled with electron capture detection.[16,17]

Accuracy (recovery of analyte). The recovery study conducted in the Assay 1 (Table III) presented values for analyte recovery between 74.1 and 99.8 %, while the MBAA compound showed lower recovery values for the three concentration levels, followed by TBAA. The other HAAs showed recovery percentages close to 100 %. The obtained values in the afternoon remained close to 100 %, showing good accuracy of the method, with the exception of MBAA and TBAA for the concentration of 30 μg L^{-1}. For all concentration values, the analyte recovery percentage increased in relation to the morning period. The obtained average recovery percentage for the surrogate standard solution was 92.9 % with an *RSD* of 0.73 %. The measures between the two periods had similar recovery values, which indicate that the method has good accuracy during the same day.

Recovery assay using spiked water samples. The recovery values obtained for the nine HAAs corresponded to 73.3–107.3 % for the Esperança samples, 69.9–96.3 % for the Z7 samples and 70.9–94.6 % for the Z3 samples. These values are considered satisfactory, since they are within the acceptable range (70–130 %) proposed by the USEPA 552.3 method.[15]

Determination of HAAs in treated water samples from different locations

The obtained values of the HAAs concentrations and the concentrations for the sums of three different haloacetic acids (HAA_5, HAA_7 and HAA_9) are presented in Table IV. The HAAs that were present in the highest concentrations in potable water samples from Maringá were DCAA and TCAA in the collecting points of Z3 and Esperança, respectively. This tendency regarding the greater abundance of these two acids in potable water was also registered by other researchers.[18,19]

TABLE IV. HAAs concentration (μg L^{-1}) in drinking water samples of the city of Maringá; Results expressed as mean ± standard deviation for analysis in three replicates. Means followed by different superscript letters (a) in same column are significantly different according to the Tukey test ($p < 0.05$); * indicates the locations supplied by artesian wells. Nd: not detected; Nq: not quantified; HAA5 = ([MCAA]+[DCAA]+[TCAA]+[MBAA]+[DBAA]), HAA7 = ([HAA5]+ +[BCAA]+[BDCAA]) and HAA9 = ([HAA7]+[CDBAA]+[TBAA])

Sample	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA
Z3	Nq	0.55 ± 0.03^{a}	4.9 ± 0.5^{a}	6.3 ± 0.4^{b}	1.89 ± 0.04^{a}	0.67 ± 0.04^{a}
Z3*	Nq	Nq	0.42 ± 0.06^{de}	0.21 ± 0.03^{d}	Nq	Nq
Z7	0.45 ± 0.05^{c}	0.51 ± 0.02^{a}	3.5 ± 0.5^{bc}	6.2 ± 0.5^{b}	1.64 ± 0.08^{ab}	0.63 ± 0.03^{a}
Z7*	Nd	0.27 ± 0.02^{b}	0.22 ± 0.01^{e}	0.31 ± 0.05^{d}	Nq	Nq
Z1	0.62 ± 0.08^{b}	0.54 ± 0.03^{a}	3.0 ± 0.7^{c}	3.8 ± 0.6^{c}	1.3 ± 0.5^{bc}	0.38 ± 0.02^{bc}
Vitória	0.58 ± 0.05^{b}	0.51 ± 0.01^{a}	4.5 ± 0.4^{ab}	4.6 ± 0.6^{c}	1.6 ± 0.4^{ab}	0.46 ± 0.09^{bc}
Esperança	0.75 ± 0.06^{a}	0.53 ± 0.08^{a}	3.6 ± 0.4^{bc}	8.0 ± 0.5^{a}	2.0 ± 0.2^{a}	0.52 ± 0.06^{ab}
WTP	Nd	Nq	1.6 ± 0.5^{d}	1.2 ± 0.2^{d}	1.0 ± 0.2^{c}	0.37 ± 0.07^{c}
Sample	BDCAA	CDBAA	TBAA	HAA_5	HAA_7	HAA_9
Z3	1.44 ± 0.09^{b}	0.72 ± 0.06^{a}	Nq	12.4 ± 0.7^{ab}	15.8 ± 0.7^{a}	16.5 ± 0.6^{a}
Z3*	Nq	Nd	Nd	0.63 ± 0.07^{d}	0.63 ± 0.07^{d}	0.63 ± 0.07^{d}
Z7	2.1 ± 0.2^{a}	Nq	Nd	11.3 ± 0.7^{ab}	15.1 ± 0.7^{a}	15.1 ± 0.7^{a}
Z7*	Nq	Nd	Nd	0.80 ± 0.05^{d}	0.80 ± 0.05^{d}	0.80 ± 0.05^{d}
Z1	0.9 ± 0.1^{c}	0.43 ± 0.04^{b}	Nd	8.32 ± 1.03^{c}	10.5 ± 1.0^{b}	10.9 ± 1.0^{b}
Vitória	1.9 ± 0.3^{a}	0.62 ± 0.02^{a}	Nd	10.7 ± 0.8^{bc}	14.1 ± 0.9^{a}	14.8 ± 0.9^{a}
Esperança	1.95 ± 0.07^{a}	0.41 ± 0.09^{b}	Nq	13.3 ± 0.7^{a}	17.2 ± 0.7^{a}	17.7 ± 0.7^{a}
WTP	0.35 ± 0.07^{d}	Nq	Nq	3.2 ± 0.6^{d}	4.6 ± 0.6^{c}	4.6 ± 0.6^{c}

The increase in the DCAA quantity in the Z3 sample in relation to the sample that was collected at the WTP may be explained by the distance that the water must travel after it leaves the station until it reaches its final destination. Along the way, a greater quantity of this acid is produced. Another reason may be the fact that Z3 is one of the oldest neighborhoods of the city and thus, by use

of older pipes, the DCAA-producing reaction is favored. However, all samples showed concentrations of haloacetic acids within the limit imposed by the USEPA.[15] Samples from artesian wells (Z3* and Z7*) showed smaller amounts of haloacetic acids when compared with the other samples. The reason for this could the differences in the substances added to complete treatment in relation to the municipal treatment plants, as well as in the lower amount of organic matter present.

PCA analysis

Principal components analysis (PCA) analysis was used to provide an overview of the relationships between the analyzed HAAs and the region from where the samples were collected. For this, a data set of 8×11 was used. The 8 sample collection points were the matrix lines and the 8 haloacetic acids which were determined in the samples, as well as the sums HAA_5, HAA_7 and HAA_9, constituted the matrix columns. PCA decomposes the data into separate sets of scores and loadings for the samples and variables, and the whole data variability is explained in order to provide a clear and more interpretable visualization of the structure of the data in a reduced dimension. The variables investigated were measured on different scales and hence, an auto-scaled data matrix was used, which allowed the variance of all variables to be identical in the first instance. The two principal components explained 99.79 % of all variance in the data. The entire data set was visualized using a biplot (combined scores and loadings plot for the two components) which is shown in Fig. 1.

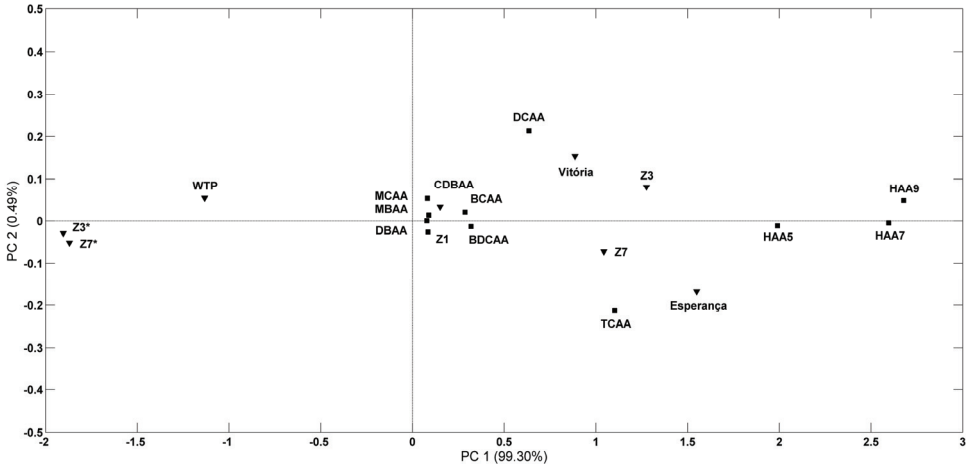

Fig. 1. Biplot graph from the results of the scores and loadings. The squares refer to the haloacetic acids and their sums and the triangles refer to the sample collection points.

Through the analysis of Fig. 1, it could be noticed that the samples of artesian wells (Z3* and Z7*) were the closest to the sample which was collected at

the water treatment plant (WTP), while belonging to the same Cartesian quadrant. The reason may be related to the fact that they were the samples with the lowest concentrations of haloacetic acids. It could be perceived that in Fig. 1 DCAA and TCAA were the closest HAAs regarding the HAAs sums HAA_5, HAA_7 and HAA_9. From the sum of their contributions (Table III), it could be noted that they were the most abundant haloacetic acids, especially in samples collected from Z3 and Esperança.

CONCLUSIONS

The performed optimization analysis for haloacetic acids determined by the GC–MS method was shown to be effective regarding the separation and quantification of nine HAA-me, within a relatively short analysis time. The method exhibited great response linearity, as well as limits of detection and quantification in the order of μg L^{-1}.

By using the SIM acquisition mode, greater analyte sensitivity and selectivity was obtained, with baseline reduction, increase in the signal/noise ratio value and elimination of interfering peaks. In addition, good method accuracy was shown in the repeatability test, in which low values of the relative standard deviation were obtained. The recovery tests showed that the extraction and derivatization methods were efficient, with acceptable values for the obtained concentration level.

The HAA_5, HAA_7 and HAA_9 levels obtained for the treated water samples collected from the city of Maringá remained below the maximum acceptable limits determined by the regulating authorities.

SUPPLEMENTARY MATERIAL

Regulations related to water purification and additional experimental details is available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

ВАЛИДАЦИЈА И ПРИМЕНА GC–MS МЕТОДЕ ЗА ОДРЕЂИВАЊЕ ХАЛОСИРЂЕТНЕ КИСЕЛИНЕ У ПИЈАЋОЈ ВОДИ

LUCAS U. R. CHIAVELLI[1], LUANA C. FIGUEIREDO[2], RAFAELA T. R. ALMEIDA[1], THIAGO CLAUS[1], SWAMI A. MARUYAMA[1] и WILLIAN F. COSTA[1]

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Постројења за третман вода хлором или натријум-хипохлоритом, током дезинфекционог процеса, обезбеђују одсуство патогних оргнизама у води. Ипак, хлор може реаговати са органском материјом и довести до формирања потенцијално карциногених спо-

редних производа, као што су халосирћетне киселине (HAA). Неколико земаља регулише нивое ових киселина у води. Стога, се њихове концентрације морају пратити са највећом могућом тачношћу. У том циљу, валидирана је метода гасане хроматографије са масеном спектрометријом (GC–MS) и примењена за одређивање HAA у узорцима вода јавног сервиса града Maringá, Paraná State у Бразилу. Блиске *recovery* вредности мерења из два периода у току дана, указују на високу тачност методе. Границе детекције (LOD = 0,42 mg L^{-1}) и квантификације (LOQ = 1.40 mg L^{-1}) су задовољавајуће за анализу дихлорсирћетне киселине (DCAA). *Recovery* вредности за девет халосирћетних киселина су у опсегу 69,9–107,3 %. Добијена је добра репродутивност у два периода анализе у току дана, с обзиром на то да су добијене сличне вредности релативне стандардне девијације (RSD).

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