JOURNAL of QASSIM UNIVERSITY FOR SCIENCE
©2023 Qassim University [E-ISSN: 1658-9610]
Vol. 2, Issue 1, pp 94-106 (Aug 2023)
JQUS

Development of method for the determination of HAA_5 in Drinking water by in-situ acidic methanol esterification and GC–MS analysis

Bechir Hammami[1,2,*], Sulaiman Abdulaziz Aldakhil[1], Hanan Mohammed A Flayh Almodibri[1], Ahmed Ali M AlShehri[1], Abuzar EAE Albadri[1], Ibrahim A. Alhagri [1,3]

[1] Department of Chemistry, College of Science, Qassim University, Buraidah 51452, Saudi Arabia.
[2] Laboratory of Heteroatom Organic Chemistry (UR 11ES29), Department of Chemistry, Faculty of Sciences of Bizerte, University of Carthage, 7021, Zarzouna, Tunisia
[3] Department of Chemistry, Faculty of Sciences, Ibb University, Ibb 70270, Yemen
*Corresponding author: b.hammami@edu.qu.sa

Abstract

Disinfection by-products (DBPs) in drinking water are formed when natural organic matter (NOM) that remains after initial treatment reacts with disinfectants, such as chlorine or chloramines. Haloacetic acids (HAA) are of health concern organic pollutants that can be formed as DBPs of water by chlorination. In this study, the use of acidic methanol esterification followed by gas chromatography with mass spectrometry detection (GC-MS) was approved for the determination of the five haloacetic acids (HAA_5) in water. The main advantage of this method is the use of acidic methanol as the derivatization agent as an alternative of the dangerous diazomethane. The mean percent recovery of HAA_5 derivatization was about 87%. The detection of limits (LOD) of the method is low than 0.1 $\mu g.L^{-1}$. The proposed method has good repeatability; precision was calculated as relative standard deviation RSD% of 7.8–10.5. The proposed method can be used for the determination of HAA_5 in drinking water.

Keywords: Chlorination. Disinfection by-products. Drinking water. Haloacetic acids. acidic methanol esterification

Introduction

Most municipal water supply systems use a form of chlorine for drinking water disinfection. Although chlorination has demonstrated its effectiveness in eliminating the problem of the presence of micro-organisms in water, it is, in turn, responsible for a problem of water contamination. This new contamination leads to the formation of disinfection by-products (DBP). The discovery of chloroform ($CHCl_3$) in chlorinated drinking water [1, 2] was the trigger for many studies conducted on chlorine and its by-products. These studies demonstrate the presence of various categories of DBPs, the main one being the class of trihalomethanes (THMs).

These by-products are likely to form by reaction between the natural organic matter of the water and the oxidants used to disinfect drinking water: chlorine, chloramines, ozone, chlorine dioxide. The type of oxidant or the combination of oxidants used during the treatment of drinking water determines the nature of the disinfection by-products in the distributed water [3].

Nearly 600 DBPs have been identified to date and the majority families have been regularly studied in drinking water networks [4]. Among these, trihalomethanes (THMs) and haloacetic acids (HAAs) represent about 30% of the total mass of DBPs [5,6].

Of all these DBP families, THMs are generally the most frequently and most abundantly found in disinfected water [7]. HAAs are found most of the time in second place in importance, but it is very common to see the concentration of HAAs approaching and even exceeding that of THMs [8]. It all depends, of course, on the type of water and the disinfection conditions. These two classes of DBP being the most important, the present work will focus more on the HAA family. HAAs belong to the family of halogenated aliphatic carboxylic acids. It should be understood that when present in drinking water at normal pH values, they are actually found there as salts, and they be called acetates [9,10]. There are nine HAAs in total, they are classified as monohaloacetic acids (MXAA or XHAA) (monochloroacetic acid (MCAA) and monobromoacetic acid (MBAA)), dihaloacetic acids (DXAA or X_2HAA) (dichloroacetic acid (DCAA), dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA)) and trihaloacetic acids (TXAA or X_3HAA) (trichloroacetic

acid (TCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA) and tribromoacetic acid (TBAA)).

Therefore, the US Environmental Protection Agency (US EPA) have set a maximum contamination level (MCL) of 60 $\mu g.L^{-1}$ for HAA_5 (MCAA, DCAA, TCAA, MBAA, and DBAA) [11], and maximum contaminant levels 80 $\mu g.L^{-1}$ for total THM concentrations in drinking water [12]. The European Union [13] has set MCL levels 100 $\mu g.L^{-1}$ for total THM concentrations. While, The World Health Organization (WHO) has published guidelines for MCAA, DCAA and TCAA and guidelines for each of the four THM species [14].

Haloacetic acids represent the largest class of non-volatile chlorination by-products. HAAs are generally difficult to determine due to their strong acidic and hydrophilic character. Therefore, efforts should be made to develop rapid and accurate analytical methods for monitoring the level, behavior and distribution of HAAs in water.

Some studies have used the analysis of HAAs by high performance liquid chromatography (HPLC) [15], by ion chromatography (IC) [16] and by capillary electrophoresis (CE) [17]. These methods do not require derivatization but they are not suitable for drinking water samples due to their low sensitivity and selectivity compared to gas chromatography (GC) methods. In fact, most analytical methods reported so far involve GC, either with electron capture detection (ECD) [18] or coupled mass spectrometry (GC-MS) [19,20]. Typically, prior to GC analysis, HAAs are first pre-concentrated by liquid-liquid or solid-phase extraction and then derivatized into their methyl or ethyl esters to render these acids volatile enough to be analyzed by GC. At the same time or after the derivatization, the methyl or ethyl esters -produced by derivatization- are often separated by liquid-liquid extraction (LLE) [21], by liquid-phase micro-extraction (LPME) [22], by hollow fiber membrane liquid-phase micro-extraction (HFLPME) [23] or by solid-phase headspace-mode micro-extraction (HS-SPME) [24,25].

Among these methods are those of the United States Environment Agency (US EPA). These are EPA Method 552.1, EPA Method 552.2, EPA Method 552.3 [26-28]. In these methods, the HAAs are extracted from the water sample using either methyl ether or methyl tert-butyl ether (MTBE) or anion exchange resins, and then they are converted into their methyl esters by diazomethane or by esterification with methanol in an acid medium. All of these methods use GC with electron capture detection (ECD) and are generally reliable and accurate with LODs for the nine HAAs

lower than µg.L^{-1}. Alternatively, mass spectrometric detector (MS) is a universal detector employed not only for the quantification but for the identification of the majority of pesticides in complex matrix samples

This paper presents the determination of haloacetic acids in water by esterification followed by gas chromatography (GC)-mass spectrometry detection (MS) analysis. The present method shows some advantage that is the use of acidic methanol instead the most widely used derivatization agent for haloacetic acids is diazomethane, which is a hazardous substance. Thus, the sensitive and simple developed method in this current work can be applied to the analysis of haloacetic acids in water matrix of several bottled and tap water sources. Moreover, this study will allow effective monitoring of HAAs which should allow a well understanding of HAAs and therefore, lead to optimization of water treatments and better control of these DBPs.

Experimental

Instrumentation

The chromatographic separations were carried out on a gas chromatograph (Agilent Technologies 7890B) equipped with GC MS detector (Agilent Technologies 7000C GC/MS Triple Quad). A DB-5MS (5% phenyl, 95% methyl polysiloxane) fused silica capillary column (30 m x 0.25 mm I.D.) (J&W Scientific, Folsom, CA, USA) with 0.25 µm film thickness was used, with helium as carrier gas, at a linear velocity of 34 cm s^{-1}. The temperature program was 40°C (held for 1 min) to 60°C at 20°C min^{-1} , to 120°C (held for 3 min) at 5°C min^{-1} and finally up to 280°C (held for 10 min) at a rate of 25°C min . Injector temperature was maintained at 250°C and splitless injection mode (2 min) was used. The mass range was from m/z 27 to m/z 260 at 0.8 s/scan with ionization time of 500 ms.

Chemicals and reagents

The studied haloacetic acids (MCAA, DCAA, TCAA, MBAA and DBAA) and their methyl esters were obtained as individual products from Fluka (Buchs, Switzerland) with a purity greater than 98%. 2,3-dibromopropanoic acid and 1,2-dibromopropane, used as surrogate and internal standard, respectively, for EPA method 552.2 were obtained from Supelco (Bellefonte, PA, USA). Analytical grade methanol and sulfuric acid were supplied by Scientific Fisher (Loughborough,

UK), while methyl tert-butyl ether for residue analysis and sodium sulphate anhydrous were purchased at Aldrich. The water used for the preparation of the aqueous reference solutions is Milli Q water quality (Millipore, Bedford, MA).

Standard solutions

The HAAs in standard reference solutions of 1000 $mg.L^{-1}$ were prepared by weighing in Milli Q water. The mixed solutions of the standards were prepared each week and the intermediate standard solutions of 10-100 $mg.L^{-1}$ were prepared in water before each analysis. All solutions were stored in the dark at 4°C and warmed to room temperature before use.

The calibration solutions were prepared by doping Milli Q water with the intermediate standard solution in appropriate volumes.

Sample collection

All samples were collected in 200ml amber glass bottles with PTFE septa and polypropylene caps. Ammonium chloride (NH_4Cl) used as a dechlorination agent to stop the formation of chlorination products was added to the sample at a concentration of 100 $mg.L^{-1}$. All samples were transported to the laboratory, transferred to the refrigerator at 4°C away from light and analyzed within 2 days of collection.

Sample preparation

EPA Method 552.2 was used in the analytical HAA_5 determination of the proposed protocol with same modification [25]. The different steps of this method are shown schematically in Figure 1. According to this protocol, the surrogate is added to 40 ml of tap water placed in a 100 ml flask. The pH is adjusted to a value below 0.5 with sulfuric acid, then sodium sulphate and copper sulphate are added. The extraction solvent (4 mL of MTBE) is added and the stoppered flask is stirred for a few minutes. The extract is then placed in a 15 mL conical test tube to which 1 mL of a solution of sulfuric acid in methanol at 10% (v/v) is added. Subsequently, the tube is closed and placed in a water bath at 50°C for 2 h. After cooling, the mixture is neutralized with 4 mL of a saturated solution of sodium bicarbonate. After recovery of the organic phase, its volume is adjusted to 1 mL and the internal standard is added to it and finally it is kept in an amber bottle until the final step of the analysis by GC.

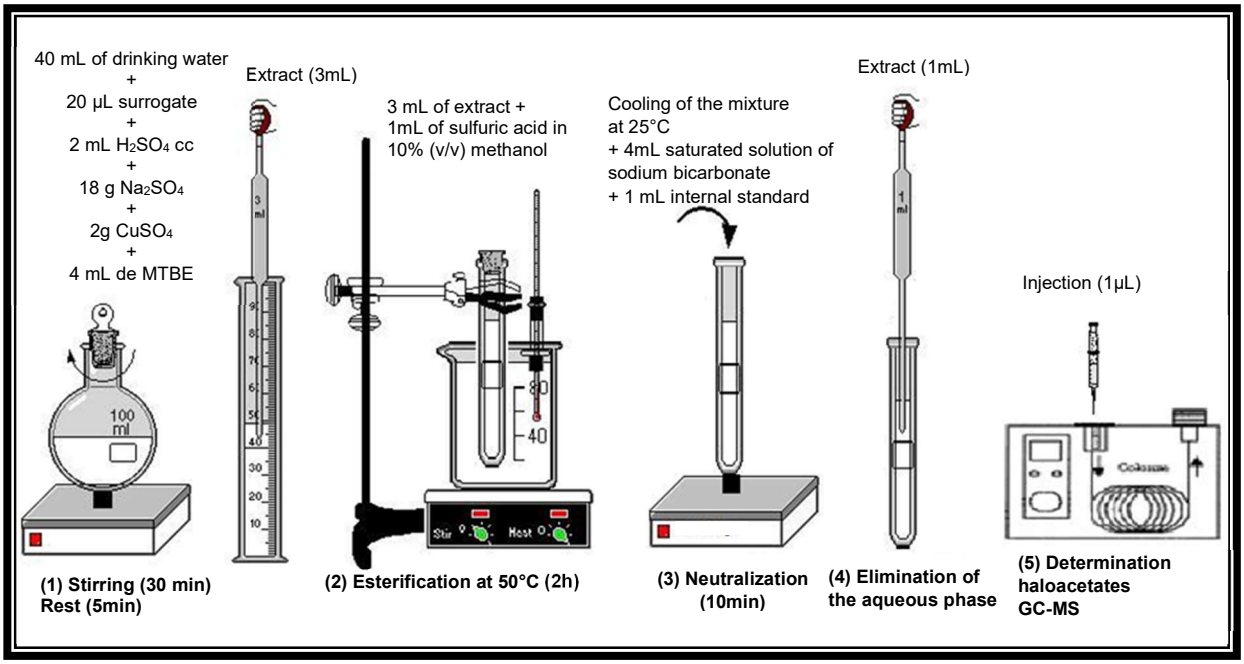

Fig. 1. Sample preparation for the analysis of haloacetic acids.

Results and discussions

Haloacetic acids represent the largest class of non-volatile chlorination by-products. HAAs are generally difficult to determine due to their strong acidic and hydrophilic character. Therefore, efforts should be made to develop rapid and accurate analytical methods for monitoring the level, behavior and distribution of HAAs in water. All the methods reported in the literature use, after extraction of the HAAs, a chromatographic technique as shown in Figure 2. Some studies have used the analysis of HAAs by high performance liquid chromatography (HPLC), by ion chromatography (IC) and by capillary electrophoresis (CE). These methods do not require derivatization but they are not suitable for drinking water samples due to their low sensitivity and selectivity compared to gas chromatography (GC) methods. In fact, most analytical methods reported so far involve GC, either with electron capture detection (ECD) or coupled to mass spectrometry (GC-MS). Typically, prior to GC analysis, HAAs are first pre-concentrated by liquid-liquid or solid-phase extraction and then derivatized into their methyl or ethyl esters to render these acids volatile enough to be analyzed by GC.

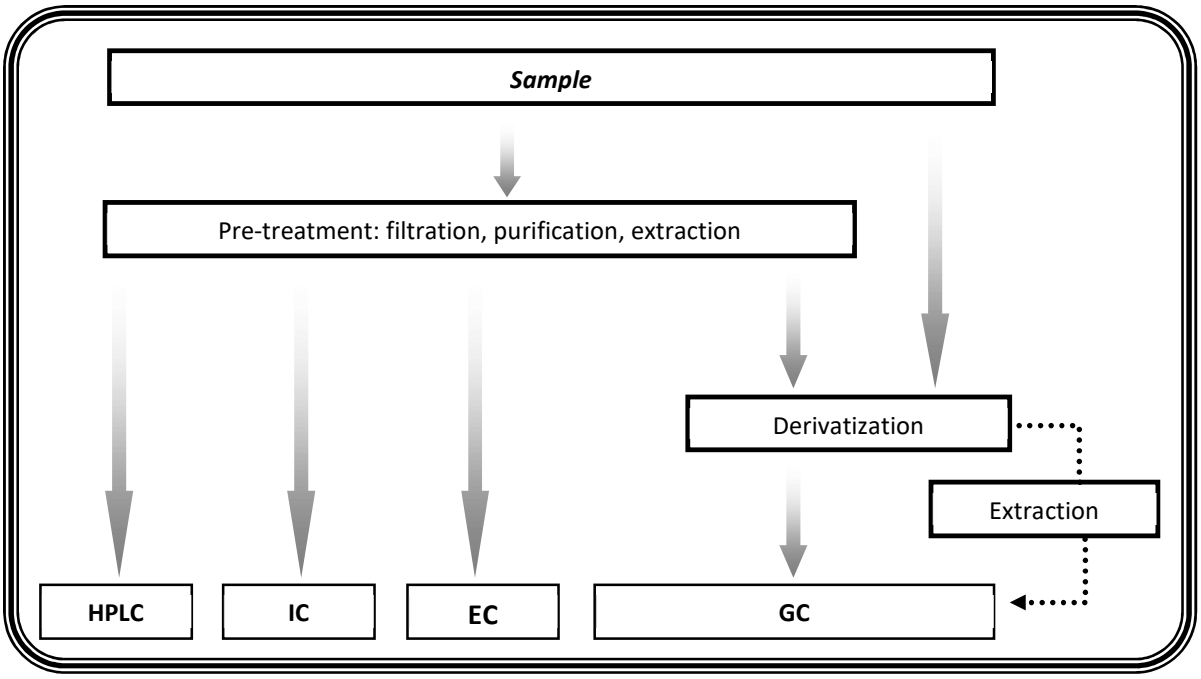

Fig. 2. General scheme for the extraction and analysis of haloacetic acids in an aqueous medium

The method of derivatization of haloacetic acids developed in this work includes a step of extraction of the acids by a solvent then esterification followed by an LLE and finally the chromatographic analysis. The yield of the esterification was followed by the evolution of the area of the chromatographic peaks of the corresponding methyl esters obtained from the different HAA_5 after their final extraction.

Recovery of the method

The acidic methanol technique used to methylate the HAA_5, termed Fisher esterification, is an acid-catalyzed equilibrium reaction that proceeds through an SN2 reaction intermediate. The reaction can be driven towards ester formation by the addition of a large molar excess of methanol or by increasing the reaction temperature.

The recovery of the acidic methanol esterification method has been estimated at three concentration levels for each haloacetic acid derivative. Stock solutions in MTBE were diluted in ultrapure water to obtain solutions with concentrations ranging from 5 to 25 µg/L. Calibration

curves of high linearity were obtained in all cases ($R^2 \geq 0.99$). An example of GC–MS chromatogram of the extract of a standard solution of the HAA_5 is illustrated in Figure 3.

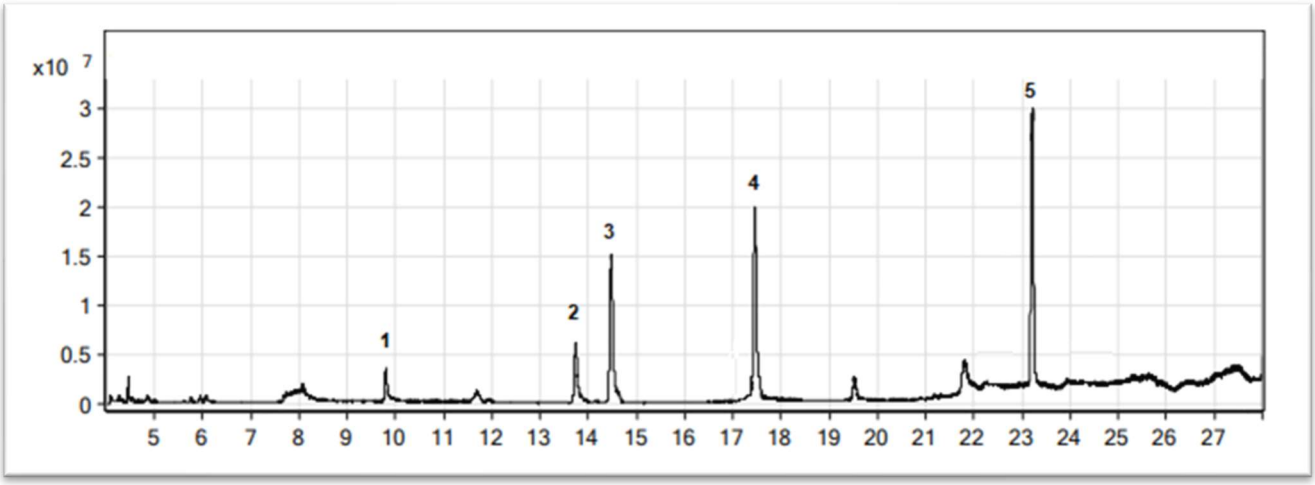

Fig. 3. GC–MS chromatogram of a standard solution of haloacetic acids 100 μg.L^{-1}. (1-MCAA, 2-MBAA, 3-DCAA, 4-TCAA, 5-DBAA)

Evaluation of the method

The acidic methanol esterification method had acceptable recoveries for all compounds tested. The recoveries generally ranged from 65% (MCAA at concentration 25 μg.L^{-1}) to 108% (DCAA at concentration 1 μg.L^{-1}).

The recoveries of the present method are comparable to those reported by previous research [29], who used diazomethane for derivatization. On the contrary, in the case of the research who also used diazomethane [30], problems with MCAA were observed, due to low ECD signal for this compound, and the LOD for DBAA, DCAA, MBAA and TCAA ranging from 0.28 to 0.75 μg.L^{-1}. The LOD with the acidic methanol esterification are also lower for DCAA and DBAA (0.02 μg.L^{-1}) [31], who applied the acidic methanol esterification method reported recoveries comparable to diazomethane method except for MCAA. Poor recovery for this compound was also observed in other work [32]. From Table 1, it can be observed that recoveries tend to decrease with increasing concentration of haloacetic acids.

Table 1

Mean recovery, relative standard deviation of the acidic methanol esterification GC–MS method at five concentration levels (n = 3 replicates)

HAA	Concentration µg/L	Recovery RSD%	Concentration µg/L	Recovery RSD%	Concentration µg/L	Recovery RSD%
MCAA	5	96.2 (4.6)	10	84.8 (11.8)	25	65.3 (8.9)
DCAA	1	108.3 (10.1)	15	98.5 (9.6)	25	85.2 (4.8)
TCAA	1	106.2 (8.4)	10	102.1 (3.2)	20	100.5 (7.6)
MBAA	5	91.2 (12.5)	10	80.2 (2.8)	20	85.3 (10.1)
DBAA	1	95.5 (5.2)	15	75.8 (6.6)	25	77.8 (9.6)

Analytical parameters

The optimized procedures were evaluated with respect to precision, linear range and limits of detection (Table 2). The precision of the method was estimated by carrying out five independent extractions of the studied compounds from MilliQ water at various spiked levels ranging from 10 to 50 µg/L under the optimized conditions. The acquired results illustrated that relative standard deviations values are acceptable, as they were about 10%. To evaluate the linearity of the method, a calibration study was performed by spiking Milli Q water with studied analytes in tested concentration ranges from 5 to 100 $\mu g.L^{-1}$. The correlation coefficients in linear range of each analyte are presented in Table 2. In brief, the R^2 coefficients can be considered good ($R^2 > 0.990$). The LOD for each compound was calculated by the signal to noise ratio S/N = 3. The LODs found were between 0.02 and 0.2 $\mu g.L^{-1}$.

Table 2.

Retention time, Linear ranges, correlation coefficients (R^2), limits of detection (LOD) and precision (n=5) of HAA_5 in water samples determined by GC-MS

Compound	Retention time (min)	Linear range (µg/L)	R^2	LOD (µg/L)	Precision		
					target value (µg/L)	Mean (µg/L)	% RSD
MCAA	9.799	5–100	0.991	0.26	50	10.33	9.7
MBAA	13.724	5–100	0.996	0.04	10	5.16	10.2
DCAA	14.471	5–100	0.995	0.02	20	20.8	10.5
TCAA	17.454	5–100	0.990	0.04	10	10.28	7.8
DBAA	23.209	5–100	0.994	0.05	20	20.03	8.2

Conclusions

The monitoring of HAA can be achieved with sensitive, reliable and reproducible analytical methods. The developed analytical method in this study for the measurement of HAA_5 in water is the methylation of the HAA followed by quantification with GC-MS, with a detection limits low than 0.1 $\mu g.L^{-1}$. High correlation coefficients were obtained for calibration lines of standard esters mixtures (> 0.990) and the relative standard deviation no more than 10%. The main advantage of this method is that acidic methanol is used as the derivatization agent instead of the hazardous diazomethane. The recoveries percent were high with low detection limits for the five haloacetic acids. For each HAA_5, the mean recovery value of esterification, expressed as a percentage of the true value, was in the range of 80-120% and the relative standard deviation were less than 20%. For these compounds that responds these criteria, performance is considered acceptable. Furthermore, the preconcentration operating conditions in this work made it possible to extract the HAA_5 from drinking water with satisfactory recoveries. This study represents a contribution for the easiest evaluation of HAAs in water and provides data that may be useful for toxicologists, survey of the levels of HAA_5 in Saudi Arabia drinking water and the establishment of specific regulation.

References

[1] W. Wang, Y. Ma, Y. Zhou, H. Huang, W. Dou, Environmental Geochemistry and Health (2021), 43, 4315–4328. https://doi.org/10.1007/s10653-021-00917-y.

[2] L. Wulff, E. Inniss, T. Clevenger, Journal of Water Resource and Protection (2013), 5, 28-34. DOI: 10.4236/jwarp.2013.58A004

[3] F. H. Frimmel, J. B. Jahnel, Formation of haloforms in drinking water, in Handbook of Environmental Chemistry, Springer-Verlag, Berlin Heidelberg (2003), 5, Part G, pp. 1–19. DOI:10.1007/978-3-540-44997-3_1

[4] K. Grob and H. Frank, "Chloroacetic acids in rainwater," Environmental Science and Technology (1996), 30(7), 2340– 2344. https://doi.org/10.1021/es9507776.

[5] C. P. Weisel, H. Kim, P. Haltmeier, J. B. Klotz, Environ. Health Perspect., Exposure estimates to disinfection by-products of chlorinated drinking water (1999), 107, 103. DOI: 10.1289/ehp.99107103.

[6] O. Hoyer, Water Supply, Monitoring raw water quality and adjustment of treatment processes – experiences at the wahnbach reservoir (1998), 16, 143. DOI:10.1016/S0273-1223(98)00008-0.

[7] S. W. Krasner, M. J. McGuire, J. G. Jacangelo, N. L. Patania, K. M. Reagan, E. M. Aieta, J. Am. Water Work Assoc., The Occurrence of Disinfection By-Products in US Drinking Water (1989), 81, 41.

[8] P. C. Singer, A. Obolensky, A. Greiner, J. Am. Water Work Assoc., DBPs in Chlorinated North Carolina Drinking Waters (1995), 87, 83. https://doi.org/10.1002/j.1551-8833.1995.tb06437.x

[9] U.S. EPA (Environmental Protection Agency des États-Unis), Addendum to drinking water criteria document for monochloractic acid and trichloroacetic acid (final). Office of Science and Technology, Office of Water, U.S. EPA, Washington, DC, juillet 2003b.

[10] EC (European Commission), Monochloroacetic acid (MCAA) environmental part. Scientific Committee on Toxicity, Ecotoxicity and the Environment, Directorate General Health and Consumer Protection, EC, Brussels, 2003. [11] US EPA, National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts, Final Rule, Vol. 63, No. 241, US EPA, Washington, DC 1998, pp. 69390–69476.

[12] WHO, Guidelines for Drinking-Water Quality, First Addendum to Third Edition, Recommendations, Vol. 1, WHO, Geneva 2006.

[13] WHO, Revision of the WHO Guidelines for Drinking Water Quality, WHO, Geneva 1991.

[14] US EPA, Disinfectants and Disinfection Byproducts: Proposed Rule, US EPA, Washington, DC 1994, pp. 38668–38829.

[15] D. Kou, X. Wang, S. Mitra, J. Chromatogr. A, Continuous, on-line monitoring of haloacetic acids via membrane extraction (2004), 1055, 1–2, 63. DOI: 10.1016/j.chroma.2005.06.075

[16] M D Hernando, M Petrovic, A R Fernández-Alba, D Barceló, Analysis by liquid chromatography-electrospray ionization tandem mass spectrometry and acute toxicity evaluation for beta-blockers and lipid-regulating agents in wastewater samples, J. Chromatogr. A, (2004), 13, 1046(1-2):133-40. https://doi.org/10.1016/j.chroma.2004.06.102.

[17] W. Ahrer, W. Buchberger, Determination of haloacetic acids by the combination of non-aqueous capillary electrophoresis and mass spectrometry, Fresenius J. Anal. Chem. (1999), 365(7), 604. DOI:10.1007/S002160051530.

[18] A. D. Nikolaou, S. K. Golfinopoulos, M. N. Kostopoulou, T. D. Lekkas, Determination of haloacetic acids in water by acidic methanol esterification–GC–ECD method, Water Research, (2002), 36, 4, 1089-1094. https://doi.org/10.1016/S0043-1354(01)00300-1

[19] M. Berg, S. R.Muller, J. Muhlemann, A. Wiedmer, R. P. Schwarzenbach, "Concentrations and Mass Fluxes of Chloroacetic Acids and Trifluoroacetic Acid in Rain and Natural Waters in Switzerland," Environ. Sci. Technol., (2000), 34, 13, 2675. doi:org/10.1021/es990855f.

[20] M. N. Sarrion, F. J. Santos, M. T. Galceran, Solid-phase microextraction coupled with gas chromatography–ion trap mass spectrometry for the analysis of haloacetic acids in water, J. Chromatogr. A, (1999), 859(2), 159. https://doi.org/10.1016/S0021-9673(99)00873-0.

[21] E. T. Urbansky, Techniques and methods for the determination of haloacetic acids in potable water, J. Environ. Monit., (2000), 2(4), 285-91. DOI: 10.1039/b002977g.

[22] M. J. Cardador, M. Gallego, Analytical technologies in the biomedical and life sciences. Determination of haloacetic acids in human urine by headspace gas chromatography mass spectrometry, Journal of chromatography. B, (2010),1; 878(21): 1824-30. DOI:10.1016/j.jchromb.2010.05.022.

[23] P. Varanusupakul, N. Vora_adisak, B. Pulpoka, In situ derivatization and hollow fiber membrane microextraction for gas chromatographic determination of haloacetic acids in water., Anal. Chim. Acta, (2007), 598(1), 82. DOI:10.1016/J.ACA.2007.07.025.

[24] B. Hammami, Models for predicting HAA5 formation as a function of pH, chlorine dose and UV254 in a drinking water system, Egypt. J. Chem. (2022), 65(8), 11-19. DOI:10.21608/ejchem.2021.78017.3816.

[25] B. Hammami & M. R. Driss, Development of dry derivatization and headspace solid-phase microextraction technique for the GC-ECD determination of haloacetic acids in tap water, Journal of Analytical Chemistry, (2013), 68, 671–679. DOI:10.1134/S1061934813080054.

[26] U.S. EPA 552.1 (Environmental Protection Agency des États-Unis). Methods for the determination of organic compound in drinking water – Supplement II. EPA-600/R-92/129. U.S. EPA, Cincinnati, OH. 1992.

[27] U.S. EPA 552.2 (Environmental Protection Agency des États-Unis). Methods for the determination of organic compound in drinking water – Supplement III. EPA-600/R-95/131. U.S. EPA, Cincinnati, OH. 1995.

[28] U.S. EPA 552.3 (Environmental Protection Agency des États-Unis). National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; National Primary and Secondary Drinking Water Regulations: Approval of Analytical Methods for Chemical Contaminants, U.S. EPA, Washington, DC, 2003.

[29] M. Matucha, J. Rohlenová, S. T. Forczek, H. Uhlířová, M. Gryndlerc, K. Fuksovád, Chemosphere, (2006), 63(11),924-1932. https://doi.org/10.1016/j.chemosphere.2005.10.014.

[30] Chen WJ, Weisel CP. Halogenated DBP concentrations in a distribution system. J AWWA 1998;90(4):151–63. DOI:10.1002/j.1551-8833.1998.tb08418.x.

[31] Y. Xie, D. A. Reckhow, D. C. Springborg. Analyzing HAAs and ketoacids without diazomethane. J AWWA, (1998) ;90(4):131–8. https://doi.org/10.1002/j.1551-8833.1998.tb08416.x.

[32] B. Cancho, F. Ventura, M. Galceran. Behavior of halogenated disinfection by-products in the water treatment plant of Barcelona Spain. Bull. Environ. Contam. Toxicol., (1999), 63, 610–7. https://doi.org/10.1007/s001289901024.