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SUPPLEMENTARY MATERIAL TO

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

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REGULATIONS RELATED TO WATER PURIFICATION

The Brazilian health ministry ordinance No. 518 dictates that the maximum free chlorine value in water is 5 mg L^{-1} and after the disinfection, the treated water must contain a minimal free residual chlorine content of 0.5 mg L^{-1}, being obligatory for the maintenance of at least 0.2 mg L^{-1} in any supply chain point.[1]

Due to the toxicity haloacetic acids (HAAs) as chlorine-generated disinfection By-products (DBPs), the US Environmental Protection Agency (USEPA) promulgated in 1998 the first stage of Disinfection By-products Regulation (Stage 1 D/DBPR),[2] which established a maximum contaminant level of 60 μg L^{-1} for the sum of the concentrations of five haloacetic acids (HAA_5), *i.e.*, monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA). It is stated in this regulation that DCAA should never be present and the concentration of TCAA should not exceed 30 μg L^{-1}. The 2nd stage of the USEPA regulation was based on the 1st stage, but with new targets for the maximum TCAA and MCAA levels of 20 and 70 μg L^{-1}, respectively. Another alternative proposal was to reduce the maximum HAAs level to 30 μg L^{-1}.[3]

The World Health Organization establishes maximum MCAA, DCAA and TCAA levels of 20, 50 and 200 μg L^{-1}, respectively.[4]

The Federal-Provincial-Territorial Committee in Drinking Waters of Canada established an acceptable maximum concentration of 80 μg L^{-1} for the sum of HAA_5 (MCAA, DCAA, TCAA, MBAA and DBAA) in consumption water.[5]

In Brazil, the national health ministry established an allowed maximum value of 80 μg L^{-1} for the sum of seven HAAs in drinking waters: MCAA,

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DCAA, TCAA, MBAA, DBAA, bromochloroacetic acid (BCAA) and bromodichloroacetic acid (BDCAA).[6]

Due to the large interest in monitoring and controlling the high levels of HAA found in waters for consumption in the United Kingdom, the European Union considers a regulation that establishes a limit of 80 μg L^{-1} for the sum of the same HAAs as cited above, plus chlorodibromoacetic acid (CDBAA) and tribromoacetic acid (TBAA).[7]

EXPERIMENTAL DETAILS

Sampling

Samples were collected from different points in the city of Maringá, Paraná State, Brazil. Five samples came from the potable water distribution system destined to the public supplying (Z1, Z3, Z7, Vitória and Esperança), two samples were from artesian wells (Z3* and Z7*) and one from the water treatment plant (WTP) station of the city, in total 8 samples. The samples were collected in 50 mL amber glass bottles each containing 5.0 mg of ammonium chloride (to convert the free chlorine residual in the sample matrix to combined chlorine, which does not react further to produce additional HAAs at significant concentrations and protect against microbiological degradation). Before sample collection, the water was run off for 3 min to discard the stopped fraction in the plumbing. After collection, the bottles were closed, manually agitated for 15 s and maintained at 6 °C for 48 h.[8]

Reagents and standards

Haloacetic acid methyl esters (HAME). methyl monochloroacetate: 60.22 mg L^{-1}, methyl dichloroacetate: 60.46 mg L^{-1}, methyl trichloroacetate: 19.85 mg L^{-1}, methyl monobromoacetate: 40.31 mg L^{-1}, methyl dibromoacetate: 20.11 mg L^{-1}, methyl tribromoacetate: 198.2 mg L^{-1}, methyl bromochloroacetate: 39.65 mg L^{-1}, methyl bromodichloroacetate: 39.70 mg L^{-1}, methyl chlorodibromoacetate: 100.0 mg L^{-1}, methyl-2,3-dibromopropanoate: 99.10 mg L^{-1} (surrogate methyl ester); the 2,3-dibromopropanoic acid standard solution: 1000 mg L^{-1} (surrogate used to monitor extraction efficiency) and the 1,2,3-trichloropropane internal standard (IS): 1000 mg L^{-1}. All solutions were acquired from AccuStandard®. A standard solution composed of nine HAAs (2000 mg L^{-1} each) was acquired from Sigma–Aldrich®. Ultrapure water (Milli-Q system, Millipore Corp., Bedford, MA, USA) was used in all analyses.

Optimization of the separation of the compounds

Programming of the chromatographic column oven. Aiming at an improvement of the chromatographic resolution, tests of the programming of the column oven temperature were executed. The tests provided significant improvements in the separation of the components in the samples and, therefore, they allowed the use of an adjusted heating slope for the separation. Using standard HAA-me and IS solutions in concentrations between 40–400 μg L^{-1} and 40 μg L^{-1}, respectively, the best programming of the GC oven temperature was evaluated in order to achieve the chromatographic separation. The best obtained conditions were: initial temperature of 35 °C for 1 min, raised to 43 °C at a rate of 5 °C min^{-1}, held for 16 min, increased to 95 °C at a rate of 10 °C min^{-1}, held for 3.4 min, with a final increase to 140 °C at a rate of 30 °C min^{-1}, which was held for 1 min. The total chromatographic separation time was 29.7 min.

Injector temperature. A standard HAA-me (P) solution containing the IS was analyzed in order to verify the influence of the injector temperature on the relative areas of the HAA-me

peaks. The injector temperature was varied from 170 to 230 °C and a decrease in the obtained P/IS signal was observed for temperatures higher than 200 °C. This decrease could be related to the thermal decomposition of HAA-me, whereby debromated HAAs and halomethanes could be generated.[9] Thus, the chosen injector temperature was 200 °C.

Carrier gas flow. The helium gas flow (carrier gas) was evaluated with the objective of improving the chromatographic separation. The following flow rates were tested: 0.5, 0.6, 0.7, 0.8, 0.9 and 1 mL min^{-1}. For values lower than 1 mL min^{-1}, the chromatographic peaks were wider and asymmetrical, the P/IS relation diminished and the analysis time was greater. Therefore, a flow of 1 mL min^{-1} was chosen.

Split ratio. Split ratio values were evaluated in the range of 1:10–1:30 of injected sample volume. Even for the split ratio value of 1:10, the obtained chromatograms showed low signal intensity for all compounds (low signal/noise relation). Consequently, it was difficult to correlate areas of the standards P and IS, and this fact could lead to inaccurate P/IS values. Therefore, it was decided to use the splitless injection mode.

Time in splitless injection mode. The time in splitless injection mode was evaluated through its variation from 6 to 60 s. In the 20–30 s interval, the P/IS relation remained practically constant for HAA-me, while below 20 s, the P/IS relation decreased. In the splitless time near 60 s, there was an increase in the P/IS relation for the analytes, with exception of TBAA. However, widening of the chromatographic peaks of all the compounds at times higher than 48 s. This effect may have been caused due to a sample concentration increase in the column entrance. In this way, a splitless time of 30 s was selected for the method, where the P/IS ratio values were high and there was no peak enlargement was observed for any of the compound.

Identification of the compounds

For the MS identification of the compounds, the full scan acquisition mode and the selected ion monitoring (SIM) acquisition mode were compared.

Full scan acquisition mode. For each separation test of the analytes present in the HAA--me mixture, the analysis was monitored in the full scan acquisition mode. This mode allowed the analysis (scan) of an extensive range of mass/charge (m/z) ratios and, therefore, allowed a comparison of each obtained spectrum with the spectral library database. The monitored m/z ratio range was 58–260. The chromatogram obtained for the separation of HAA-me with IS in the full scan mode is shown in Fig. S-1.

The HAA-me, IS and surrogate-me retention times were: 6.06 (MCAA-me), 9.27 (MBAA-me), 10.03 (DCAA-me), 17.64 (IS), 17.88 (TCAA-me), 18.15 (BCAA-me), 23.20 (DBAA-me), 23.55 (BDCAA-me), 27.01 (surrogate-me), 27.12 (CDBAA-me) and 29.33 min (TBAA-me). The compound methyl-2,2-dichloropropanoate, which eluted in 11.93 min (Fig. S-1) is not a compound of interest because, despite being a constituent of the combined standard that was acquired from AccuStandard®, it is not a haloacetic acid.

Selected ion monitoring acquisition mode. The selected ion monitoring (SIM) acquisition mode was tested to monitor specific values of the m/z ratio regarding the fragments of each compound. In this way, greater selectivity and sensitivity could be obtained when compared to acquisition in the full scan mode, as well as an increase in the value of the signal/noise ratio. The obtained chromatogram for HAA-me separation with IS monitored in the SIM mode is shown in Fig. S-2.

When compared with the full scan mode chromatogram (Fig. S-1), it was observed that the interfering peaks did not appear on the SIM mode chromatogram. This is due to the exclu-

sive monitoring of specific fragment masses from the analyte, which enables the elimination of interfering chromatographic peaks.

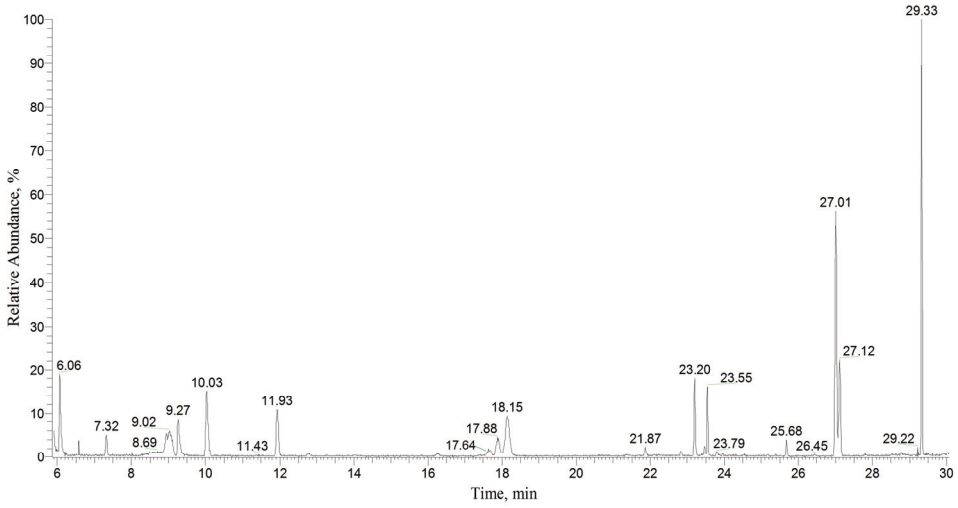

Fig. S-1. Chromatogram of a standard solution of HAA-me from 200–2000 µg L^{-1} with trichloropropane (IS) 200 µg L^{-1} in the full scan acquisition mode (*m*/*z* 58–260).

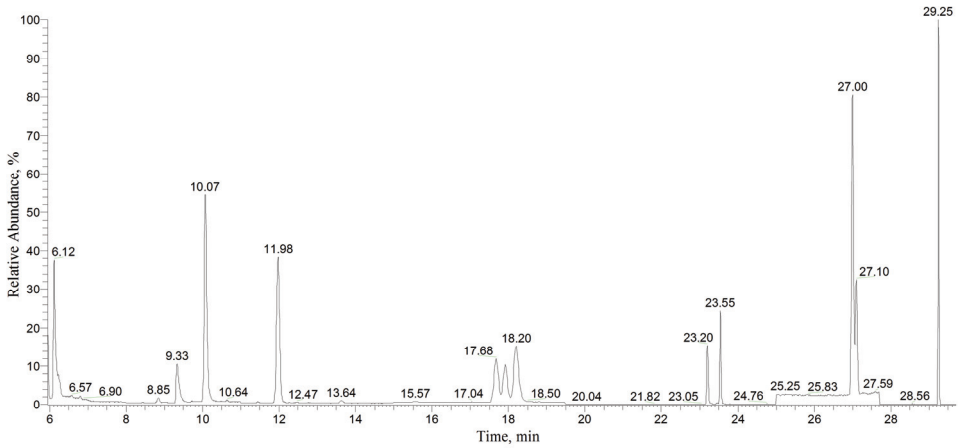

Fig. S-2. Chromatogram of 40–400 µg L^{-1} HAA-me standard solution with 40 µg L^{-1} IS using the SIM acquisition mode.

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