

# Study of iodo-haloacetic acids using SPME-GC-MS/MS in chlorinated water

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**Abstract.** The aim of the study was to develop, optimize and validate an analytical method for the simultaneous identification of iodine haloacetic acids (I-HAAs) drinking water using the technique of Gas-Chromatographic separation coupled with mass spectrometry (GC-MS/MS). The sample screening and analytes detection was performed on an Agilent 7890B gas chromatograph coupled with an Agilent 7010B triple quadrupole mass spectrometer (MS/MS). The separation of the compounds was achieved using a VF-1710 column (30m x 250mm x 0.25mm). Elution was performed with helium, 1 mL/min, with oven operating at following program: 35°C (6 min), 10 °C/min up to 220°C (6 min). For the extraction of I-HAAs from water samples, Solid Phase Microfiber Extraction (SPME) with a 1.1 mm 120 µm Divinylbenzene/Carbon Wide Range/Polydimethylsiloxane (DVB/C-WR/PDMS) fiber was used.

**Keywords:** I-HAA, SPME-GC-MS/MS analysis, drinking water

## 1. Introduction

Iodine disinfection products and especially I-HAAs are receiving increasing attention from the scientific community and water regulatory authorities due to their high toxicity compared to regulated haloacetic acids (HAAs). Because in Romania was implemented from January 2023 the newer in force legislation regarding the content of haloacetic acids in drinking water (Directive (EU) 2020/2184), it is expected that many water treatment plants will replace disinfection with chlorine in favor of chloramine disinfection. The last one procedure has the advantage to produce lower concentration of HAAs (HAA9, with chlorine and bromine), but the literature data indicate that this technology has a tendency to form numerous I-HAAs in the presence of possible traces of iodide in the water (Ackerson et al, 2020; Postigo et al, 2019; Dong et al, 2019).

Following the water disinfection process, in addition to the formation of haloacetic compounds with chlorine and bromine (Cl, Br-HAAs), the oxygenated species HOI can be formed as a result of the interaction of oxidizing agents with the iodide ions. These reacts slowly with organic

matter forming species of haloacetic acids that also contain iodine. The rapid degradation of the HOI species in the presence of chlorine, ozone or Mn oxide reduces the content of haloacetic acids with iodine (I-HAAs) in the treated water. However, by replacing these disinfection agents with chloramine, although the concentration of normalized haloacetic acids (Cl, Br-HAAs) is reduced, a much higher amount of I-HAAs is formed in the presence of the iodide ions in the water, thus resulting in a toxic effect higher due to the much higher toxicity of I-HAAs.

At the international level, the emerging risks of highly toxic disinfection by-products (DBP), such as I-HAAs, iodine-trihalomethanes (I-THMs), but also haloacetaldehydes (HALs) has been highlighted in different studies that emphasize their high toxicity (eg: the cytotoxicity of iodoacetic acid is 287 times higher than that of chloroacetic acid, quantitatively the main compounds from HAAs) (Richardson et al, 2008).

These compounds (I-HAAs), considered until now with an insignificant contribution to the total toxicity of water treated by chlorination, were identified in much higher concentrations as a result of replacing processes used for drinking water production. The iodine is present usual in small doses (Badescu et al, 2020), but also could be in high concentration as result of anthropogenic pollution (Ackerson et al, 2020). Iodine reacts with chloramine forming predominantly I-HAA and I-THM (Postigo et al, 2019).

Similarly, chlorination with technologies based on the use of peracetic acid-hydrogen peroxide mixtures, used especially in the USA, to obtain very low values of THMs and HAAs in the treated water, revealed that traces of iodine are almost completely converted into I-HAA and I-THM (Xue et al, 2017).

For the analysis of I-HAA, I-THM and HAL, the selective extraction and concentration of the analytes is particularly important (Li et al, 2022). For this purpose, XAD-2 and XAD-8 resins (Plewa et al, 2004), SPME with Polydimethylsiloxane (PDMS) fiber (Xue et al, 2017) or DVB/C-WR/PDMS fiber (Li et al, 2022) and much less

often liquid-liquid extraction (Ackerson et al, 2020) have been successfully used.

Gas-chromatographic separation can be performed on columns with medium polarity, e.g.: 5% phenyl, 30 m (Ackerson et al, 2020; Liu et al, 2017), while for detection the best performances are achieved by GC-MS/MS (Xue et al, 2017), the sensitivity of Electron Capture Detector (ECD) for I-DBP being unsatisfactory.

Until now, at the national level, no analytical methodologies or studies have been developed for the identification of I-HAL, I-THM and HAL in drinking water. Directive (EU) 2020/2184 imposes a maximum allowed value of HAAs in drinking water of 60 µg/L, THMs have an imposed limit of 100 µg/L, while for HALs there are still no imposed limits. In Romania, a study carried out in 2020 indicates the presence of iodine in surface waters (Xue et al, 2017). This type of water represent 80% of raw water used for the production water intended for human consumption.

The aim of the study was to develop a GC-MS/MS method for simultaneous identification of iodine haloacetic acids (iodoacetic acid, chloriodoacetic acid, diiodoacetic acid, iodobromoacetic acid) from water samples. The low volatility of these compounds required derivatisation by methylation, and for this purpose methanol or dimethyl sulfate in acidic condition was used. The identification of iodo-haloacetic acids was achieved using water with a standardized content of fulvic acids, treated by chlorination in the presence of the iodide ion.

## 2. Materials and methods

### 2.1. In-situ derivatization of haloacetic acids with iodine

In-situ derivatization of haloacetic acids with iodine in a standardized matrix that simulates production of drinking water by chlorination in the presence of iodide ions was carried out using the following substances: fulvic acids (from shilajit, 250 mg, concentration of 50% fulvic acids, food supplement from Zenyth), potassium iodide, sodium bicarbonate, sodium sulfite and chlorine water.

The solutions used to generate haloacetic acids with iodine were: solution of 62.5 mg/L fulvic acids, 10 mg/L KI, 10 g/L NaHCO<sub>3</sub>, 1 g/L chlorine water. For 1000 mL of solution, 100 mL of 62.5 mg/L fulvic acids solution, 0.1 mL of 10 mg/L KI solution, 10 mL of 10 g/L NaHCO<sub>3</sub> solution, 5 mL of 1 g/L chlorine water solution were used. Finally, in one liter of solution there were: 6.25 mg/L fulvic acids, 1 mg/L KI, 100 mg/L NaHCO<sub>3</sub> and 5 mg/L Cl<sub>2</sub>. The synthetic solution was subjected to chlorination for 2 h under magnetic stirring. Samples of 50 mL were taken, and the reaction was stopped with 1 g of sodium sulfite added to the sampling bottle (60 mL). The sample was added with 100 µL DMS, sealed and stirred at a constant temperature of 50°C for 30 minutes. Afterwards, the total immersion of the active surface of a DVB/C-WR/PDMS SPME fiber was carried out for 30 minutes, after which the fiber was rinsed with deionized water and dried at ambient temperature for 10 minutes, followed by the desorption stage in the GC injector.

### 2.2. GC-MS/MS method

A new GC-MS/MS analytical method was developed capable of identifying and quantifying haloacetic acids with iodine, in presence of chlorine and bromine from drinking water. The conversion of haloacetic acids into the corresponding methyl esters was achieved by treating the sample with dimethyl sulfate in situ. To isolate the corresponding esters, a DVB/C-WR/PDMS (Divinylbenzene/Carbon Wide Range/ Polydimethylsiloxane) SPME fiber was used, which showed superior analyte concentration performance compared to other types of fibers tested (DVB/DDMS and PDMS).

Because the studied molecules are small, satisfactory MS/MS transitions could not be established, which is why the identification and confirmation of the analytes was carried out in SIM (Single Ion Monitoring) mode. The optimized parameters of the chromatograph and the mass spectrometer, parameters used for detection of I-HAAs are presented in table 1.

The experimental part was applied on an Agilent 7890B Gas Chromatograph system coupled to with an Agilent 7010B triple quadrupole mass spectrometer.

**Table 1.** The optimal parameters of SPME-GC-MS/MS for the I-HAAs detection

| Derivatization and SPME                                    | GC Parameters   | MS-MS Parameters  |
|--|---|---|
| DVB/C-WR/PDMS (1.1mm Arrow) fiber<br>Film thickness: 100µm | Column VF-1701MS, 30m x 0.25mm x 0.250µm<br>Elution with He 6.0, 1 mL/min | MS in SIM mode (Single Ion Monitoring)<br>Transfer line temperature: 260 °C |
| Sample Volume: 10 mL                                       | Injector: 260°C, splitless  | Aquisition time, Dwell time: 100 msec                                       |
| Derivatization with dimethylsulfate, 100 µL                | Heating program: 35°C (6 min), 10°C/min up to 220°C (5.5 min)             |   |
| Derivatization time: 25 min                                | Total time of analysis: 30 min  |   |
| Incubation temperature: 60°C                               |   |   |
| Incubation time: 30 min                                    |   |   |
| Analyte collection method: immersion in the liquid phase   |   |   |

The chromatographic data were collected using the acquisition and control software Mass Hunter, manufacturer Agilent Technologies 7890 GC System, which was also used for data processing and identification of I-HAAs.

## 3. Results and discussions

The identification parameters of iodo-haloacetic acids in the presence of chloro- and bromo-acetic acids by mass spectrometry are presented in table 2. The identification of

I-HAA acids was carried out based on the identification of characteristic ions using the NIST spectral database.

Figure 1 shows the SIM chromatogram of a drinking water solution containing the 4 I-HAA acids.

For I-HAAs, the repeatability of the method was characterized by values of relative standard deviations (RSDr) between 7.2 and 12.2%, while for HAA9 it varied between 2.5% and 4.9%.

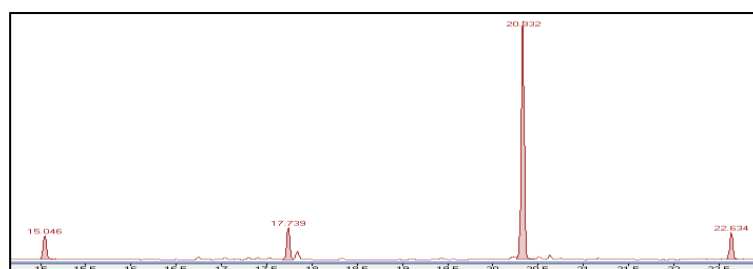
#### 4. Conclusions

The paper present a method for identification of I-HAAS compounds after derivatization in presence of chlorine and

bromine in drinking water samples at trace level using GC-MS/MS technique.

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**Figure 1.** SIM chromatogram of a drinking water solution containing the 4 I-HAAs.

**Table 2.** The identification parameters of the tested compounds

| Analyzed compound                 | Retention time, minutes | Quantification ion | Confirmation ion |
|-----------------------------------|-------------------------|--------------------|------------------|
| mono chloro methyl acetate        | 7.82                    | 108                | 79               |
| methyl monobromoacetate           | 7.95                    | 93                 | 95               |
| methyl dichloroacetate            | 11.96                   | 83                 | 85               |
| methyl trichloroacetate           | 14.82                   | 117                | 119              |
| bromo chloro methyl acetate       | 15.41                   | 129                | 127              |
| methyl dibromoacetate             | 17.36                   | 173                | 171              |
| bromo dichloro methyl acetate     | 17.62                   | 163                | 161              |
| methyl chlorodibromoacetate       | 19.57                   | 207                | 209              |
| methyl tribromoacetate            | 21.31                   | 251                | 253              |
| <b>methyl iodoacetate</b>         | 15.05                   | 200                | 73               |
| <b>chloro iodo methyl acetate</b> | 17.74                   | 234                | 79               |
| <b>methyl diiodoacetate</b>       | 20.33                   | 326                | 171              |
| <b>methyl bromiodoacetate</b>     | 22.63                   | 278                | 123              |

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