



## Fast and “green” method for the analytical monitoring of haloketones in treated water



María Serrano, Manuel Silva, Mercedes Gallego\*

Department of Analytical Chemistry, Campus of Rabanales, University of Córdoba, E-14071 Córdoba, Spain

### ARTICLE INFO

#### Article history:

Received 14 May 2014

Received in revised form 24 June 2014

Accepted 30 June 2014

Available online 8 July 2014

#### Keywords:

Haloketones

Micro liquid–liquid extraction

Large-volume injection

Programmed-temperature vaporiser

GC–MS technique

Treated water

### ABSTRACT

Several groups of organic compounds have emerged as being particularly relevant as environmental pollutants, including disinfection by-products (DBPs). Haloketones (HKs), which belong to the unregulated volatile fraction of DBPs, have become a priority because of their occurrence in drinking water at concentrations below 1  $\mu\text{g/L}$ . The absence of a comprehensive method for HKs has led to the development of the first method for determining fourteen of these species. In an effort to miniaturise, this study develops a micro liquid–liquid extraction (MLLE) method adapted from EPA Method 551.1. In this method practically, the whole extract (50  $\mu\text{L}$ ) was injected into a programmed temperature vaporiser–gas chromatography–mass spectrometer in order to improve sensitivity. The method was validated by comparing it to EPA Method 551.1 and showed relevant advantages such as: lower sample pH (1.5), higher aqueous/organic volume ratio (60), lower solvent consumption (200  $\mu\text{L}$ ) and fast and cost-saving operation. The MLLE method achieved detection limits ranging from 6 to 60 ng/L (except for 1,1,3-tribromo-3-chloroacetone, 120 ng/L) with satisfactory precision (RSD,  $\sim 6\%$ ) and high recoveries (95–99%). An evaluation was carried out of the influence of various dechlorinating agents as well as of the sample pH on the stability of the fourteen HKs in treated water. To ensure the HKs integrity for at least 1 week during storage at 4 °C, the samples were acidified at pH  $\sim 1.5$ , which coincides with the sample pH required for MLLE. The green method was applied to the speciation of fourteen HKs in tap and swimming pool waters, where one and seven chlorinated species, respectively, were found. The concentration of 1,1-dichloroacetone in swimming pool water increased  $\sim 25$  times in relation to tap water.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

The chemical disinfection of drinking water has significantly reduced the incidence of infectious waterborne disease, but reactions of disinfectants such as chlorine to natural organic matter in source water produce chemical mixtures composed of hundreds of different disinfection by-products (DBPs) [1–4]. Approximately, 600–700 DBPs have been reported in the literature although most of them continue being unregulated to date [1]. Haloketones (HKs), which belong to the unregulated volatile fraction, can be formed in water treated with chlorine, chloramines and chlorine dioxide, as well as ozone–chlorine and ozone–chloramine combinations [3,5]. 1,1-Dichloroacetone (1,1-DCA), 1,3-dichloroacetone (1,3-DCA) and 1,1,1-trichloroacetone (1,1,1-TCA) have been the common HKs identified in treated water and the effect of several parameters on their formation have been studied extensively [6–8]. Moreover,

these HKs (with other DBPs) have been detected at low concentrations in treated water of four water treatment plants as well as from eight representative points of the distribution network of Athens [9–11]. The World Health Organisation has concluded that there is not sufficient data to be able to propose guideline values for any chloroacetone [12], even though they were included in the Information Collection Rule of the United States Environmental Protection Agency (EPA) due to their potential health effects and unclear exposure doses [13]. Therefore, to date, the concentration of these HKs in drinking water has not been regulated in any country. From the toxicological studies of HKs [12,14,15] that have been reported, it is known that their mutagenic activity decreases as chlorine substitutions at the C-1 and C-3 positions increase, with the exception of 1,1,1-TCA [12]. Dermal absorption has been established as an important route of exposure for potentially toxic volatile DBPs, including HKs, during bathing in chlorinated drinking water [16]. In addition, Xu and Weisel [17] have suggested that a potential inhalation exposure to HKs takes places after 10 min in a shower, which contributes more than 10% of their daily ingestion doses. As regards this topic, the same authors measured 1,1-DCA and 1,1,

\* Corresponding author. Tel.: +34 957 218 614; fax: +34 957 218 614.  
E-mail addresses: [qa1gafem@uco.es](mailto:qa1gafem@uco.es), [mercedes.gallego@uco.es](mailto:mercedes.gallego@uco.es) (M. Gallego).

1-TCA concentrations in the breath of human subjects after showering or bathing, reporting that both HKs were valid to evaluate inhalation exposure, but not for dermal absorption evaluation because of the low permeability of these compounds through human skin [18,19].

Nowadays there is a growing interest in the family of chlorinated and brominated acetones because the information about these compounds is scarce due to their lack of commercial chemical standards until nearly the 2000. In this context, mass spectral library databases for brominated acetones were available much later than for chlorinated ones [20]. Hence, the data on the occurrence, stability and analysis of the HKs in drinking water are very limited [4,21,22], and only one contribution includes ten HKs [21]. Generally the determination of HKs in water relies on a modified EPA Method 551.1, based on liquid–liquid extraction (LLE), which is commonly used to determine halogenated volatile organic compounds (VOCs), including 1,1-DCA and 1,1,1-TCA, in drinking water [23]. EPA Method 551.1 has been used in a study on the occurrence of up to ten HKs in drinking water, but it provides low sensitivity (LODs, 100–500 ng/L) [21]. Nikolaou et al. [24] have assayed and compared different sample preparation techniques [LLE, purge-and-trap (P&T) and manual static headspace (HS)] in combination with the gas chromatography–electron capture detector (GC–ECD) and GC–mass spectrometry (MS) for the simultaneous determination of fifteen VOCs in drinking water, including 1,1-DCA, 1,3-DCA and 1,1,1-TCA. With respect to these three HKs, this study concluded that: (i) neither P&T–GC–MS nor HS/GC–MS can be used for the determination of 1,3-DCA since it was not recovered; and (ii) LLE was the best analytical technique to achieve the highest sensitivity for the determination of the three HKs, reaching average limits of detection (LODs) of 50 or 120 ng/L using ECD or MS detection, respectively. Modern approaches to sample preparation for determining VOCs in water are more dedicated to the proposal of miniaturised extraction or solventless methods. Thus, solid-phase microextraction (SPME) methods have been developed for the two most common chlorinated acetones based on either HS–SPME–GC–MS [25] (LOD of 100 and 180 ng/L, for 1,1-DCA and 1,1,1-TCA, respectively) or manual HS–SPME/GC–ECD (LOD of 0.3 and 8.3 ng/L, for 1,1-DCA and 1,1,1-TCA, respectively) [26]. With regard to the SPME technique, it is noteworthy that these methods suffer from the well-known problems involved in SPME methods, such as the poor reproducibility of the fibre, or limited extraction capacity caused by the low amount of sorbent material [27]. From the above-mentioned, it is possible to conclude that: (i) the EPA Method 551.1 was usually employed for this purpose although it needs large volumes of organic solvents and is time consuming; among studies based on EPA Method 551.1, only one of them included up to ten HKs [21]; and (ii) only one miniaturisation technique (SPME) has been applied to determine 2 HKs [25,26].

In recent years there has been a clear trend towards greener analytical methods for reducing, or even eliminating the use of organic solvent; the developments and perspectives of liquid phase microextraction has recently been reviewed [28]. Micro liquid–liquid extraction (MLLE) is a simple technique which uses smaller sample volume than standard LLE, lowers the cost of analysis by reducing both the amount of extractant (sensitivity increase) and the amount of waste, following the trend towards “Green Chemistry”. In addition, the use of the programmed-temperature vaporised-based large-volume injection coupled to GC–MS enable the injection of almost all the organic extract into the GC, which yields a further increase in the sensitivity of the method since HKs are present in drinking water usually at concentrations below 1 µg/L. Thus, the aim of this research was to develop the first MLLE method, based on EPA Method 551.1, for the determination of a large number of HKs (14 species) at nanogram per litre levels in treated water. Furthermore, a comprehensive study was performed

on several of the dechlorinating agents used for the preservation of finished tap water. Finally, the MLLE method proposed was validated with EPA Method 551.1 by analysing tap and swimming pool waters—it is the first time that HKs have been quantified in pool water.

## 2. Materials and methods

### 2.1. Standard solutions

Chloroacetone (CA, 95%), 1,1-dichloroacetone (1,1-DCA, 99%), 1,3-dichloroacetone (1,3-DCA, 95%), 1,1,1-trichloroacetone (1,1,1-TCA, 99%), 1,1,3-trichloroacetone (1,1,3-TCA, 87%) and 1,2-dibromopropane (IS, internal standard) were purchased from Sigma-Aldrich (Madrid, Spain). 1,1-Dibromoacetone (1,1-DBA, 90–95%), 1,1,3,3-tetrachloroacetone (1,1,3,3-TeCA, 90–95%), 1,1,1,3-tetrachloroacetone (1,1,1,3-TeCA, 85–90%), 1,1,1-tribromoacetone (1,1,1-TBA, 90–95%), 1,1-dibromo-3-chloroacetone (1,1-DB-3-CA, 85–90%), 1,1-dibromo-3,3-dichloroacetone (1,1-DB-3,3-DCA, 90–95%), 1,1,3-tribromoacetone (1,1,3-TBA, 90–95%), 1,3-dibromo-1,3-dichloroacetone (1,3-DB-1,3-DCA, 90–95%) and 1,1,3-tribromo-3-chloroacetone (1,1,3-TB-3-CA, 85–90%) were supplied by CanSyn (Toronto, Canada). Ethyl acetate, *n*-hexane, methyl *tert*-butyl ether (MTBE) and sulphuric acid were purchased from Merck (Darmstadt, Germany), whereas ammonium sulphate, anhydrous sodium sulphate, L-ascorbic acid, sodium thiosulphate pentahydrate and ammonium chloride were supplied by Panreac (Barcelona, Spain).

Stock standard (1.0 g/L) and cumulative (0.1 g/L) solutions of each HK were prepared in MTBE and stored at –20 °C. More diluted individual or cumulative solutions were prepared daily in mineral water (free of DBPs) at the microgram per litre level.

### 2.2. PTV–GC–MS conditions

Analyses of the HKs were performed on a programmed-temperature vaporised (PTV)–GC–MS instrument (Agilent Technologies, Palo Alto, CA, USA) consisting of an HP 7890A series gas chromatograph equipped with a G2619A Septumless Head PTV injector and an HP 5975C mass selective detector (Triple-Axis Detector). The PTV was operated in solvent vent mode using a multi-notch deactivated liner (Part No. 5183-2041). A large-volume injection (LVI) of 50 µL was performed (vent time, 0.01 min; vent flow, 10 mL/min; pressure, 0 psi; purge, 60 mL/min at 2 min), for which the inlet temperature was programmed from 45 °C (0.01 min) to 250 °C (0 min) at a rate of 500 °C/min. The analytes were separated on an HP-5MS column (30 m × 0.25 mm × 0.25 µm) from Agilent, with the following oven temperature program: initial temperature 40 °C (held 3 min), ramped at 10 °C/min until 100 °C, then at 120 °C/min to 150 °C (held 2 min), and finally at 120 °C/min to 250 °C. Helium (6.0 grade purity) was employed as the carrier gas at a flow rate of 1 mL/min, and the solvent delay was 4.5 min. The mass spectrometer was operated in electron impact mode using an ionisation voltage of 70 eV. The transfer line and ion source temperatures were set at 250 °C. The analyses were performed in synchronous selected ion (SIM)/scan mode which allowed both SIM and full scan data to be collected in a single run. A full scan (40–400 amu) was used for identification and SIM for quantification, selecting the characteristic ions in each case. The characteristic ions for the fourteen HKs studied are shown in Table 1.

### 2.3. Sample preparation and stability

Samples were collected in 125 mL amber glass bottles with polytetrafluoroethylene (PTFE) screw caps and adjusted at pH

Download English Version:

<https://daneshyari.com/en/article/7612777>

Download Persian Version:

<https://daneshyari.com/article/7612777>

[Daneshyari.com](https://daneshyari.com)