



Direct determination of trace-level haloacetic acids in drinking water by two-dimensional ion chromatography with suppressed conductivity



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ABSTRACT

During the treatment process of drinking water, disinfectants (chlorine, ozone, chlorine dioxide) react on water containing organic matter and bromide to produce disinfection by-products at trace levels. Among them, five of the nine existing halo-acetic acids (HAAs) are commonly found in drinking water (monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and Trichloroacetic acid (TCAA)), including four classified in the 2B IARC group of potential carcinogens (BCAA, DBAA, DCAA, TCAA). With respect to drinking water quality, guidelines are proposed by WHO (2006) and water quality standards are imposed in many countries such as less than 100 µg/L for the sum of the five HAAs by US EPA (1998) and Canadian Health Department (2008). For this purpose, two analytical methods are commonly used, GC/MS with derivatization and LC/MS, UV or conductivity. A new method, based on two-dimensional ion chromatography (IC 2D) with suppressed conductivity is proposed. This method presents the main advantage of offering a quick implementation compared to GC or LC methods: direct injection, slight maintenance, lower cost of investment, by leading to good performances (specificity and sensitivity). The use of two different selectivity columns, and the fractionation on the first dimension canceling interferences, improves the specificity. The sensitivity is enabled by interfacing a preconcentration column between the two different internal diameter columns. The analytical conditions are optimized for the analysis of nine HAAs. The performances of the method are evaluated. The optimized method applied to natural water samples demonstrates its ability to quantify HAAs at trace levels in drinking water.

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1. Introduction

1.1. Formation, occurrence and regulation of disinfection by-products

During the disinfection step of drinking water treatment process, disinfectants (chlorine, ozone, chlorine dioxide) react on water containing organic matter and bromide to produce disinfection by-products (DBPs). Among the six hundred substances identified, haloacetic acids (HAAs) and trihalomethanes (THM) represent the two major classes and thirty percent on a weight basis [1,2].

Among the HAAs, nine bromo and/or chloroacetic acid combinations are possible: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCBA), and tribromoacetic acid (TBAA).

Five of these nine HAAs (MCAA, DCAA, TCAA, MBAA, DBAA) were commonly found in drinking water in the US, with a mean concentration

of 23 µg/L [3]. In other countries, DCAA and TCAA between 2 µg/L and 12 µg/L were analyzed in Canada [4], DCAA (from 0.4 µg/L to 13 µg/L) and TCAA (from 0.6 µg/L to 11 µg/L) in drinking water in China [5], up to 49.5 µg/L for the sum of the five HAAs in tap water in Seoul [6], from 0.9 to 87 µg/L for the sum of the nine in Spain [7]. Regarding the seasonal influence, the five HAA concentrations were 1.0–38.9 µg/L in winter and 0.2–46.7 µg/L in summer, in drinking water of Taiwan, DCAA and TCAA being the two major HAAs (around 30% and 26% respectively) [8].

In the International Agency for Research on Cancer classification [9], four of the nine HAAs are classified in the 2B group as possibly carcinogenic to humans (BCAA [10], DBAA [11], DCAA [12], TCAA [13,14]). The World Health Organization (WHO) proposes guidelines for drinking water as a point of departure for national authorities to determine drinking water regulations and standards [15]. WHO has established guidelines for chlorinated HAAs (MCAA: 20 µg/L; DCAA: 50 µg/L; TCAA: 200 µg/L), but not for brominated HAAs. The national authorities' approaches are different according to countries. For example, on the sum of the five commonly found HAAs, the US EPA has fixed regulation at 60 µg/L in 1998 [16] and Health Canada has fixed recommendation at 80 µg/L in 2008 [17]. In Europe, HAAs are not yet standardized despite an increasing demand of sanitary surveys as for example, campaigns in four drinking water systems in France [18].

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1.2. State of the art of analytical methods

HAA analysis is usually performed by GC or LC techniques (Table 1). The GC methods require two steps of sample preparation, a liquid–liquid extraction (LLE) and an extract concentration [19,20]. To reduce the extraction volume during sample preparation, new techniques have been developed such as the liquid–liquid microextraction [21] and the single-drop microextraction (SDME) [22]. A recent procedure combining liquid–liquid microextraction and headspace (HS) GC may allow reducing the time of sample preparation [23]. In order to get volatile compounds, a derivatization step is carried out before injection of the extract into the gas chromatograph. Two types of detectors are available: (i) the electron capture detector (ECD), specific for halogenated substances, has a good sensitivity but requires training and protection precautions against the radioactive source and (ii) the mass spectrometer (MS) provides better security identification. The main advantage of GC methods is a good sensitivity with limits of detection (LOD) between 0.01 and 1.2 µg/L according to the method and the substance, as shown in Table 1. However the sample preparation steps are heavy to run and time-consuming, which may consider GC analysis of HAAs tedious and expansive [19,20].

LC methods are divided into two categories: (i) reversed-phase liquid chromatography [24] and (ii) ion chromatography (IC) [25]. Regardless on the technique used, the sample is injected either directly or after a preconcentration step (online or offline) on a solid phase extraction (SPE) cartridge. Direct LC methods can be achieved thanks to an electromembrane extraction (EME) followed by UV detection [26] or a LC/MS/MS technique [27]. Several types of detection are available with IC methods, the most frequent being conductimetry (CD) [25], possibly with preconcentration SPE cartridge for a better sensitivity [28]. The second type of IC detection is MS, often used in tandem [29,30]. The third type of IC detection is fluorimetry (FL), associated with post-column reaction (PCR) [31]. All LC techniques avoid the tedious steps of sample treatment for GC, with LOD between 0.0007 µg/L and 35.4 µg/L as shown in Table 1. The wider

range of LOD with regard to GC is explained by the different techniques proposed for separation and detection. With GC or LC, MS detection requires more staff qualification and higher costs of investment and maintenance than the use of specific detectors, but has the advantages of more reliability and specificity. Overall the performances of all methods presented are in compliance with recommendations and regulations for water quality.

1.3. Principle of the two-dimensional ion chromatography (IC 2D)

The method proposed hereafter allows separating the nine HAAs using a two-dimensional ion chromatography separation with a conductimetric detection (IC 2D). The interest of the method is the improvement of the sensitivity (thanks to two different diameters of successive columns) and the specificity (different phases). A collection window enables the selection of anions of interest on a column concentrator during the first step (first dimension). Thus, these anions are eluted during the second step (second dimension). The two successive separations on two columns of different diameters (an analytical column and a capillary column) with a concentration step between the two columns increase the sensitivity by the square of the ratio of the two columns diameters.

2. Material and methods

2.1. Chemicals

All chemicals used to prepare HAA standard solutions were of analytical grade purity and were obtained from Merck (Darmstadt, Germany). Individual haloacetic acids DCAA, BDCAA and BCAA were obtained from Supelco (Bellefonte, PA, USA), MCAA and TCAA from Fluka (Saint-Louis, MO, USA), MBAA, DBAA and TBAA from Dr Ehrenstorfer (Augsburg, Germany) and BCAA from Aldrich (Chicago, IL, USA).

Table 1
Existing methods for HAA analysis.

Analytical technique	Sample preparation	Performances			Reference
		LOD (µg/L)	Linearity (µg/L)	Matrix	
GC/ECD or GC/MS	LLE/derivatization	TCAA: 0.05 ^a	0.5–10	Ground, tap water	[19]
GC/ECD	LLE/derivatization	0.5 ^{ab}	0.5–200	Ultra-pure water (UPW)	[20]
GC/MS	SDME/derivatization	0.1 to 1.2 ^b	0.5–20	Deionized water	[22]
HS/GC/MS	Liquid–liquid microextraction/derivatization	0.02 to 0.4 ^b	0.1–300	Mineral water	[23]
IC/CD	Reagent addition for interferences elimination	MCAA: 3.7 DCAA: 3.6 TCAA: 35.4	10–2000	Deionized water	[25]
LC/UV	EME	MCAA: 0.0007 DCAA: 0.019	5–200	Water	[26]
LC/MS/MS	Direct injection	0.16 to 8.87 ^b	0.25–100	UPW	[27]
IC/CD	Offline SPE preconcentration	MCAA: 3.5 MBAA: 1.5 DCAA: 10 DBAA: 5 TCAA: 6	Un-specified	Tap water	[28]
IC/MS/MS	SPE preconcentration	0.04 to 0.3 ^b	10–1000	UPW	[29]
IC/MS/MS	Direct injection	0.015 to 0.20 ^b	0.25–20	UPW	[30]
IC/PCR/FL	Direct injection	0.6 to 10.1 ^b	2–50	UPW	[31]

^a Limit of quantification.

^b For the 9 HAAs, according to the substance.

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