

Determination of Ten Haloacetic Acids in Drinking Water Using High-Performance and Ultra-Performance Liquid Chromatography–Tandem Mass Spectrometry

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Abstract

Haloacetic acids (HAAs) are a class of byproducts resulting from the reaction of chlorinated disinfectants with natural organic matter. These chemicals have been found in animal studies to possibly influence hepatic, reproductive, and developmental functions, and they may be mutagenic and carcinogenic. Because HAAs are hydrophilic and strongly acidic, it is a challenge to measure them at low levels. In this study, nine traditional HAAs and monoiodoacetic acid, an emerging disinfection byproduct, are analyzed in water directly. HAAs were separated on a BetaMax Acid column or a HILIC UPLC column, and they were detected by negative electrospray ionization-tandem mass spectrometry. Although the on-column limits of detection of HAAs were lower when using an HILIC UPLC column (0.08–2.73 µg/L) than when using a BetaMax Acid column (0.18 to 71.5 µg/L), to use an HILIC UPLC column, it was required to dissolve water samples in 90% acetonitrile before injection and result in sample dilution. BetaMax Acid column was found to be more suitable for the analysis of HAAs in drinking water because there was no need of sample preparation. Major species of HAAs, such as dichloroacetic acid and trichloroacetic acid, and other primary species (e.g., dibromoacetic acid, bromochloroacetic acid and bromodichloroacetic acid) can be detected using the BetaMax Acid column at concentrations higher than 1–3 µg/L.

Introduction

Disinfection byproducts (DBPs) may be produced through the reactions of disinfectants with natural organic matters in raw water. The most abundant DBPs resulting from chlorination are trihalomethanes, followed by haloacetic acids (HAAs), the next most abundant (1–3). There are nine major chlorinated and brominated acetic acids, including monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and chlorodibromoacetic acid (CDBAA) (4). Humans are less exposed to trihalomethanes than

to HAAs because they are more volatile than HAAs (boiling points ~60°C vs. boiling points ~180°C, respectively) and are usually removed during the boiling process of drinking water.

In animal studies, HAAs have been found to be toxic to liver and embryos and may be mutagenic, carcinogenic, and have reproductive effects in lab animals (5–9). The Integrated Risk Information System of the United States Environmental Protection Agency (U.S. EPA) has classified DCAA as a group B2 chemical (i.e., a probable human carcinogen) and TCAA as a group C compound (possible human carcinogen) (10,11). In addition, iodoacetic acids may be more toxic and mutagenic than chloro- and bromo-acetic acids (12).

Although the total concentrations of HAAs vary by seasons, water sources, and drinking water treatment plants, the most abundant species are usually TCAA and DCAA (13,14), making up about 80% of all HAA concentrations (13), followed by BDCAA and BCAA, which make up around 15% (13). The U.S. EPA has established a maximum contamination level of 60 µg/L for the total concentrations of five HAAs (HAA5: MCAA, DCAA, TCAA, MBAA, DBAA) (15); World Health Organization set up maximum contamination levels of DCAA and TCAA at 50 and 100 µg/L, respectively (3).

Most surveys report low-µg/L levels of HAAs in drinking water. In a study of 12 drinking water treatment plants in the US, Krasner et al. found the concentrations of the nine HAAs ranged 3–18 µg/L (16). In Canada, except at plants using chlorine as the disinfectant, concentrations were found to be lower than 50 µg/L for most HAAs (17). Analyzing tap water from 10 locations in Taiwan, Hsu found the individual concentrations of six HAAs to range from 1–13 µg/L and total concentrations to range from 5–33 µg/L (18).

The standard method of analyzing HAAs in drinking water is the U.S. EPA Method 552 (19). Because of the strongly acidic characters (pKa range 0.63–2.90) of HAAs (20,21), samples are acidified to reduce the dissociation of HAAs, which are extracted using methyl-*t*-butyl ether. The extracts are esterified with methanol to enhance the volatility of the analytes and then are concentrated under gentle nitrogen flow. The residues are then analyzed using gas chromatography–electron capture detection (GC–ECD). Although highly sensitive (0.012–0.17 µg/L), this method is time-consuming and labor-intensive. Another limita-

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