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Pentafluorobenzyl esterification of haloacetic acids in tap water for simple and sensitive analysis by gas chromatography/mass spectrometry with negative chemical ionization

Can Zhao, Yukiko Fujii, Junxia Yan, Kouji H. Harada, Akio Koizumi *

Department of Health and Environmental Sciences, Kyoto University Graduate School of Medicine, Yoshida, Kyoto 606-8501, Japan

HIGHLIGHTS

- Haloacetic acids (HAAs) levels in tap water are determined.
- Pentafluorobenzyl esterification is used for pretreatment.
- Gas chromatography/mass spectrometry with negative chemical ionization is used.
- Method has low detection limits (8–94 ng L^{-1}) and good recovery rates (89–99%).
- The HAAs concentrations are in range 0.54–7.83*f* Kg L^{-1} in Japanese tap water.

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ABSTRACT

Chlorine is the most widely used disinfectant for control of waterborne diseases in drinking water treatment. It can react with natural organic matter in water and form haloacetic acids (HAAs). For analysis of HAA levels, derivatization with diazomethane is commonly recommended as the standard methodology in Japan. However, diazomethane is a carcinogenic alkylating agent. Therefore, in this study, a safe, simple, and sensitive quantification method was developed to monitor HAAs in drinking water. Pentafluorobenzyl esterification was used for pretreatment. The pentafluorobenzyl-ester derivative was detected by gas chromatography–negative ion chemical ionization-mass spectrometry analysis with very high sensitivity for HAAs analysis. The method has low detection limits (8–94 ng L^{-1}) and good recovery rates (89–99%) for HAAs. The method was applied to 30 tap water samples from 15 cities in the Kansai region of Japan. The levels of HAAs detected were in the range 0.54–7.83 μg L^{-1}. Dichloroacetic acid, trichloroacetic acid, and bromochloroacetic acid were the major HAAs detected in most of the tap water, and accounted for 29%, 20% and 19% of the total HAAs, respectively. This method could be used for routine monitoring of HAAs in drinking water without exposure of workers to occupational hazards.

1. Introduction

In drinking water treatment, chlorine is widely used for control of waterborne diseases such as cholera, typhoid, hepatitis and gastro-intestinal illness (Morris and Levin, 1995). However, it can react with natural organic matter in water to form a variety of disinfection by-products, including trihalomethanes and haloacetic acids (HAAs) (Badawy, 1992).

There are nine HAAs commonly found in drinking water, including monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), dibromochloroacetic acid (DBCAA), and

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Abbreviations: HAAs, haloacetic acids; MCAA, monochloroacetic acid; DCAA, dichloroacetic acid; TCAA, trichloroacetic acid; MBAA, monobromoacetic acid; DBAA, dibromoacetic acid; TBAA, tribromoacetic acid; BCAA, bromochloroacetic acid; DBCAA, dibromochloroacetic acid; BDCAA, bromodichloroacetic acid; PFBBr, 2,3,4,5,6-Pentafluorobenzyl bromide; MTBE, methyl *tert*-butyl ether; GC–NCI-MS, gas chromatography–negative ion chemical ionization-mass spectrometry; MCL, maximum contaminant level; IDL, instrumental detection limit; MDL, method detection limit; MQL, method quantification limit.

* Corresponding author. Address: Department of Health and Environmental Sciences, Kyoto University Graduate School of Medicine, Yoshida Konoe, Sakyo, Kyoto 606-8501, Japan. Tel.: +81 75 753 4456; fax: +81 75 753 4458.

E-mail address: koizumi.akio.5v@kyoto-u.ac.jp (A. Koizumi).

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bromodichloroacetic acid (BDCAA) (Magnuson and Kelty, 2000). The International Agency for Research on Cancer has categorized TCAA as Group 3 (not classifiable as to its carcinogenicity in humans) despite animal tests showing that TCAA and DCAA are hepatotoxic and DCAA and DBAA adversely affecting male reproductive function (Linder et al., 1994). Both TCAA and DCAA caused substantial systematic organ toxicity, including liver and kidney damage, in rats in a 13-week subchronic study (Mather et al., 1990). In epidemiological studies, HAA exposure was significantly correlated with an increased risk of bladder (Villanueva et al., 2004) and colorectal cancers (Rahman et al., 2010).

Because of the suspected adverse health effects of HAAs, the United States Environmental Protection Agency has regulated five HAA species (HAA_5 = MCAA, DCAA, TCAA, MBAA, DBAA) to a maximum contaminant level (MCL) of 60 $\mu g\,L^{-1}$ based on a running annual average (USEPA, 1999, 2001). The World Health Organization (WHO) provides guidelines for the regulation of MCAA, DCAA and TCAA of 20, 50, and 200 $\mu g\,L^{-1}$, respectively (World Health Organization, 1993).

In Japan, sodium hypochlorite (NaOCl) is the most common primary disinfectant used in tap water treatment. Consequently, it is expected that HAAs are ubiquitous in drinking water in Japan. The Japanese Drinking Water Quality Standards for MCAA, DCAA, and TCAA are 20, 40 and 200 $\mu g\,L^{-1}$, respectively (Wakayama, 2003). However, guidelines have not been established for other HAAs and monitoring data are not available.

For chemical analysis of HAAs in tap water, derivatization with diazomethane is commonly recommended as the standard methodology in Japan. However, diazomethane is a carcinogenic alkylating agent and its use presents hazards to laboratory workers (International Programme on Chemical Safety, 1995). Acidic methanol esterification was introduced (Munch et al., 1995; Xie et al., 1998; Nikolaou et al., 2002), and widely used in Asia, Europe and North America. Even though methylester derivatives of TBAA, DBCAA and BDCAA are prone to thermal decomposition and hydrolysis in the GC injection port (Munch et al., 1995; Xie, 2001), the method has been modified to improve methylation efficiency (Domino et al., 2004; Xie et al., 2002, 1998).

Above method employs gas-chromatography/electron capture detector (GC–ECD). Mass-spectrometry (MS) technique is another method to detect target analytes qualitatively and quantitatively with fragment ions (Xie, 2001). Derivatization of HAAs to the 2,4-difluoroanilide with carbodiimide and GC–MS analysis has been described (Alaee and Scott, 1998) and adopted for the determination of HAAs in water sample. However, with this derivatization, recoveries tend to decrease with increasing concentrations of the HAAs. Reports in the literature suggest that pentafluorobenzyl bromide (PFBBr) could increase the electron capture capability of the analyte (Galdiga and Greibrokk, 1998), and enhance both the separation and detection of organic acids (Knapp, 1979). In addition, negative chemical ionization (NCI)-MS analysis for pentafluorobenzyl (PFB)-ester derivatives can provide very high sensitivities for HAAs analysis in biological samples (Jia et al., 2003).

The aim of the present study was to develop a safe, simple, and sensitive quantification method, as an alternative to the diazomethane method to monitor HAAs in drinking water. Thus, in this study we optimized PFBBr derivatization of HAAs and analyzed them using NCI-MS. In parallel with the newly developed method, HAAs levels were monitored in 30 tap water samples obtained from 15 cities in the Kansai region of Japan.

2. Materials and methods

2.1. Materials and reagents

Potassium carbonate and sodium chloride were obtained from Nacalai Tesque (Kyoto, Japan). 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr), 2,3-dibromopropionic acid (recovery surrogate), methyl *tert*-butyl ether 5000 (MTBE, HPLC grade), 11H-eicosafluoroundecanoic acid (internal standard), and 1,4,7,10,13,16-hexaoxacyclooctadecane were purchased from Wako Pure Chemical Industries (Osaka, Japan). Halogenated Acetic Acid Standard Stock Solution II was obtained from Kanto Chemicals (Tokyo, Japan). A derivatization reagent (3% PFBBr) was prepared by dissolving 300 μL of PFBBr and 100 mg of 1,4,7,10,13,16-hexaoxacyclooctadecane in 10 mL of MTBE.

All glassware was washed with detergent, rinsed with tap water and then Milli-Q (MQ, Millipore, Billerica, MA) water, and oven dried before use.

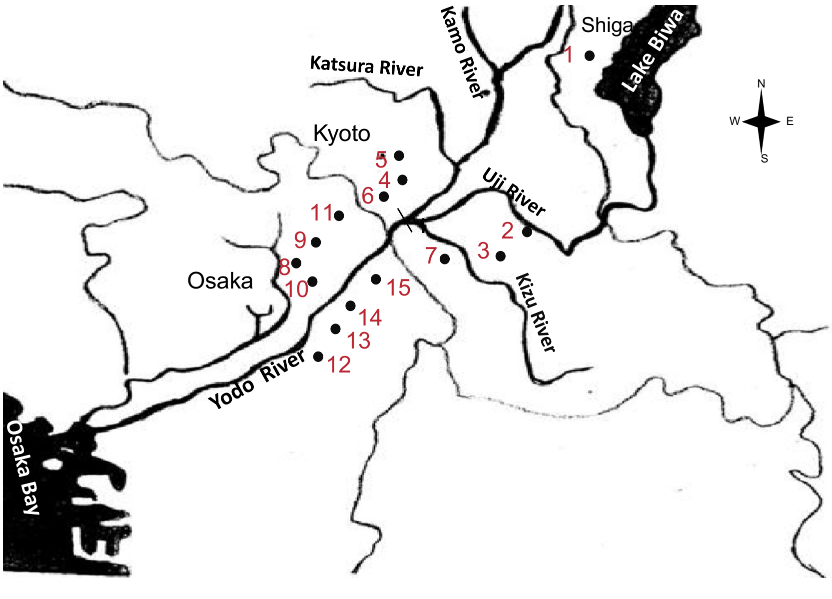

Fig. 1. Locations of water sampling sites in the Kansai region of Japan.