Science of the Total Environment 640–641 (2018) 581–590

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Determination of six iodotrihalomethanes in drinking water in Korea

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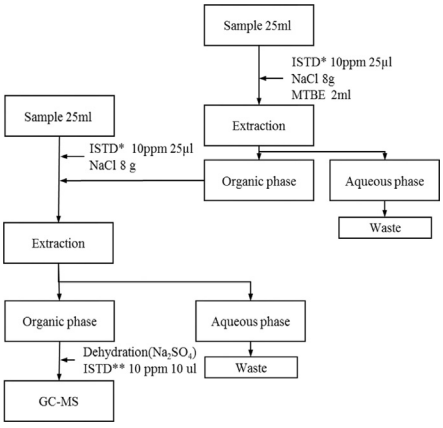
HIGHLIGHTS

- We established an LLE-GC–MS method for analysis of I-THMs in drinking water.
- The MDL of I-THMs was 0.01–0.10 ng/mL and showed a precision of <11%.
- We analyzed six kinds of I-THMs in drinking water from water purification plants in Korea.
- The samples were classified by disinfection systems, regions, seasons and water sources.

GRAPHICAL ABSTRACT

Scheme. The extraction scheme of I-THMs in drinking water.



ARTICLE INFO

Article history:
Received 23 February 2018
Received in revised form 3 May 2018
Accepted 26 May 2018
Available online xxxx

Keywords:
Iodotrihalomethanes
Drinking water
Liquid-liquid extraction
GC–MS

ABSTRACT

Trihalomethanes (THMs) are chemicals regulated by Environmental Protection Agency's first drinking water regulation issued after the passage of the Safe Drinking Water Act. Among THMs, iodotrihalomethanes (I-THMs) are produced by treating water containing iodides ion with chlorine or ozone. I-THMs are more carcinogenic and biotoxic than chlorinated or brominated THMs. The purpose of this study was to analyze of I-THMs in drinking water using the liquid-liquid extraction (LLE) method with various extraction solvents. The calibration curves ranged from 0.01 to 20 ng/mL and the correlation coefficient showed a good linearity of 0.99 or more. The method detection limit ranged from 0.01 to 0.10 ng/mL. The accuracy of the LLE method ranged from 99.43 to 112.40%, and its precision ranged from 1.10 to 10.36%. Good recoveries (71.35–118.60%) were obtained for spiked drinking water samples, demonstrating that the LLE method is suitable for the analysis of drinking water samples. Dichloroiodomethane, bromochloroiodomethane, and dibromoiodomethane were identified in drinking water collected from 70 places of water purification plants in Korea. The samples were classified by disinfection systems, regions, seasons, and water sources. The concentration of I-THMs in pre-/postchlorination facilities owing to excess chlorine usage was higher than in ozonization/postchlorination facilities. Moreover, the concentrations of I-THMs were high in the coastal region, because of the large amount of halide ions from the sea. There was no seasonal difference; however, the concentration of I-THMs in pre-/postchlorination facilities increased in spring and summer. The concentration of I-THMs in water sources was high in samples from the Geum River and the Yeongsan and Sumjin River. The concentration and detection frequency of I-THMs in Han River and Nakdong River were high in the coastal region, because of numerous pre-/postchlorination facilities and the abundance of halide ions from the ocean.

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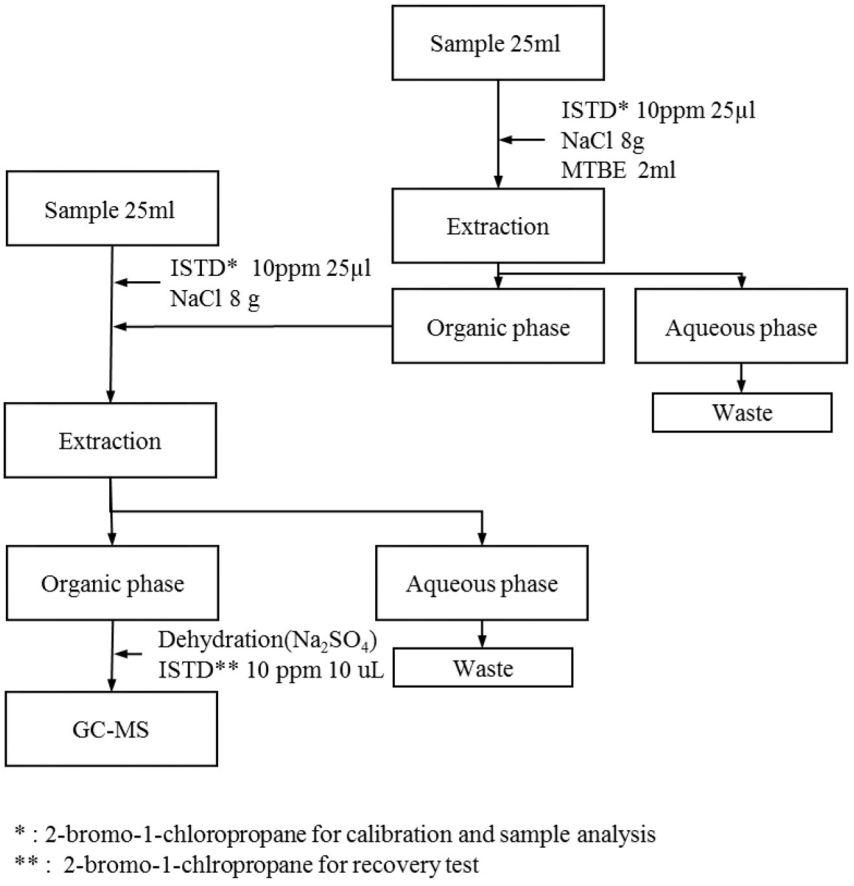
https://doi.org/10.1016/j.scitotenv.2018.05.329
0048-9697/

1. Introduction

Trihalomethanes (THMs) are compounds in which three of the four hydrogen atoms of methane are replaced by halogen atoms. Chlorine, which is used for disinfection and sterilization purposes in water treatment, produces several disinfection byproducts (DBPs) that exhibit carcinogenicity (Richardson et al., 2007; Krasner et al., 2006; Pressman et al., 2010). Among THMs, iodotrihalomethanes (I-THMs) are produced by treating water containing iodide (I^-) with chlorine or ozone (Hua et al., 2006; Hansson et al., 1987). Iodide is oxidized into hypoiodous acid (HOI) at near-neutral pH by chlorination, chloramination, and ozonation. HOI can react with organic compounds, including natural organic matter, which produces I-THMs. Generally, iodide levels in natural water are usually around 10 ng/mL (Shin et al., 1996), however, they can reach >50 ng/mL due to special geological formations or seawater intrusions (Bichsel, 2000; Von Gunten, 2003). There are six types of I-THMs: dichloroiodomethane (DCIM), bromochloroiodomethane (BCIM), dibromoiodomethane (DBIM), bromodiiodomethane (BDIM), chlorodiiodomethane (CDIM), and iodoform (IF). I-THMs have been synthesized in relation to their pharmaceutical or medicinal smell and the taste of water. I-THMs are more genotoxic and mutagenic than regulated chlorinated and brominated THMs (Plewa et al., 2004; Richardson et al., 2008). Iodo- and iodobromo-THMs are more toxic than their iodochloro analogs (Richardson et al., 2008). They can cause taste and odor problems and do not satisfy the regulatory standards for I-THMs stipulated by the US Environmental Protection Agency (USEPA) (Hatch et al., 1999; Vel Leitner et al., 1998). Furthermore, there is no approved method for analyzing the amounts of I-THMs in drinking water.

Therefore, we attempted to identify an optimal analysis method to simultaneously determine the amount of I-THMs in drinking water. Several analytical methods have been used to analyze I-THMs. Traditional liquid-liquid extraction (LLE) and headspace methods are universal. Solid-phase microextraction (SPME) has been applied for the analysis of iodinated byproducts (Cancho et al., 1999), and can achieve the required sensitivity (Cancho et al., 2000; Allard et al., 2012). The advantage of the LLE method is that selective analytes can be extracted while changing the pH and polarity of the extraction solvent. It is easier to control the background effect, as compared to other methods, and sample usage is variable. The disadvantage of the LLE method is that its sensitivity is lower than that of the headspace and SPME methods. Moreover, solvent usage causes environmental pollution. However, the same calibration in the LLE method can be applied when monitoring large numbers of samples. On the other hand, the SPME method is not suitable for many samples, because it can reduce sensitivity due to fiber contamination, and one fiber can analyze 20–30 samples. In addition, the natural concentration effect can be seen to be excellent when analyzed by the method presented in this paper. In fact, the LLE method is currently the primary method for the analysis of I-THMs in drinking water (Richardson et al., 2008; Bichsel and Von Gunten, 2000; Pressman et al., 2010; Smith et al., 2010). It has been used to extract and concentrate DBPs by U.S. EPA Method 551 (Munch and Hautman, 1995; Liew et al., 2012).

Gas chromatography-mass spectrometry (GC–MS) is capable of quantitative and qualitative analysis; however, gas chromatography-electron capture detector (GC-ECD) has better sensitivity in quantitation than GC–MS and is suitable for detecting halogen compounds.



Scheme 1. The extraction scheme of iodotrihalomethanes in drinking water.