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Application of hollow fiber liquid phase microextraction for simultaneous determination of regulated and emerging iodinated trihalomethanes in drinking water

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ABSTRACT

Trihalomethanes (THMs) are regulated disinfection by-products (DBPs) most commonly analyzed in quality control water supply due to their harmful effects on health. However, few data exist about the content of emerging iodo-trihalomethanes (I-THMs) which are present in drinking water at very low concentrations (in the order of ng L^{-1}). For this reason a two-phase hollow fiber liquid phase microextraction method for the simultaneous determination of four regulated trihalomethanes and six emerging iodo-trihalomethanes using GC-μECD and GC–MS with detection limits in the range of few ng L^{-1} has been developed. A central composite design was used to optimize conditions for simultaneous extraction. The best extraction recovery was obtained with 19.2 min at 27.1 °C and 900 rpm, without salt addition, using a supported hollow fiber membrane of 10.5 cm (0.6 mm id) and 1-octanol as acceptor phase. The limits of detection for the regulated THMs and I-THMs were 3–44 ng L^{-1} and 1–3 ng L^{-1}, respectively. The calibration curves showed good linearity ($R^2 > 0.995$) and good repeatability (3–22%). The relative recoveries in water were between 96.5% and 105.2%. The method was applied for the simultaneous determination of trihalomethanes in supply water samples from seven water distribution systems (WDS) in the Huelva area, located at the southwest Spain, which use different water-treatment processes. The highest concentrations of I-THMs, particularly CHBrClI and $CHCl_2I$, were detected in water treated with advanced treatment process using pre-ozonation, however these compounds were not detected or decreased along distribution system. In the samples of treated water with conventional treatment, using pre-oxidation by permanganate and distribution network, $CHCl_2I$, CHBrClI, $CHClI_2$, $CHBrI_2$ and CHI_3 were detected at very low concentrations (1–18 ng L^{-1}). Finally, in water samples from underground origin without oxidation treatment, in which only disinfection with sodium hypochlorite was applied, I-THMs were not detected.

1. Introduction

Drinking water chlorination plays an important role in preventing pathogen contamination that causes water-borne diseases. However, chemical disinfection with chlorine leads to the formation of disinfection by products (DBPs) due to reaction with natural organic matter (NOM), which can cause potential health problems [1]. Epidemiologic investigations have demonstrated the association between exposure to DBPs present in drinking water and cancer (bladder [2], colon [3] stomach, pancreas, kidney and rectum) [4,5], as well as adverse birth outcomes [6,7]. THMs exposure may also contribute to increased risk of Hodgkin and non-Hodgkin lymphoma [8] and spontaneous abortion. Up to now, about 600–700 DBPs have been identified in drinking water [1], but only few DBPs have been evaluated for adverse effects. Therefore, only a limited number of regulations and guidelines have been established for DBPs, which include four trihalomethanes (THMs: chloroform, bromoform, bromodichloromethane, and chlorodibromomethane) and five haloacetic acids (HAAs: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid and dibromoacetic acid) [9,10].

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Iodinated DBPs (I-DBPs) include iodo-acids and iodo-trihalomethanes that have been identified in drinking water from ng L^{-1} to low μg L^{-1} levels. I-THMs have been described as powerful cytotoxics [11], and recent studies have demonstrated that iodinated DBPs had more cytotoxic and genotoxic effects than their brominated and chlorinated analogues, due to the stronger leaving potential of iodine atom. Iodoform (CHI_3) was considered the most cytotoxic compound, and chlorodiodomethane ($CHClI_2$) as the most genotoxic I-THMs species [12]. Additionally, mammalian cell toxicity results provided evidence for the toxicity of iodinated DBPs because iodoform (CHI_3) was 60 times and 146 times more cytotoxic than bromoform ($CHBr_3$) and chloroform ($CHCl_3$), respectively [13]. In addition to their toxicity, I-THMs have very low odor and taste thresholds, especially iodoform (CHI_3), which at concentrations above 0.1 μg L^{-1} water provides a characteristic medicinal smell [14].

Different analytical methods have been reported for analysis of regulated THMs in drinking water, but gas chromatography (GC) coupled with electron capture detection (ECD) or mass spectrometry (MS) are widely used. ECD detector is generally more sensitive than mass spectrometry (MS) for halogenated organic compounds, although MS detector is more selective to confirm the compounds detected in the samples [15].

Many of these methods study critically analyte extraction techniques or the introduction of the sample into the GC. Conventional liquid–liquid extraction (LLE) [16–19], purge and trap [20–24], direct aqueous injection (DAI) [25–27], static headspace (HS) [28–30], solid-phase microextraction (SPME) [31,32], solid-phase extraction [33], headspace solid-phase microextraction (HS-SPME) [34–37], liquid-phase microextraction (LPME) [38,39], headspace-liquid-phase microextraction (HS-LPME) [40,41], hollow fiber membrane (HF-LPME) [42,43] and dispersive liquid–liquid microextraction (DLLME) [44,45], have been used to monitor regulated THMs species in drinking water.

Low concentrations of I-THMs in water samples require inclusion of optimal pre-concentration step before the gas chromatography analysis, such as liquid–liquid extraction (LLE) [12,46,47]. An alternative method to extract and concentrate analytes from water samples is the use of solid-phase microextraction (SPME) [47–49].

Moreano-Rosero et al. compared HS-SPME, HF-LPME and HS extraction for determination of trihalomethanes in drinking water by gas chromatography electron capture detector and mass spectrometry detection. As result, the HF-LPME–GC–ECD method proved to be the most sensitive for determination of regulated THMs compounds, with a very high concentration factor, low LOD, good accuracy and precision [43].

Due to the increased interest in monitoring the occurrence of I-DBPs in water, analytical methods for the simultaneous quantification of chloro, bromo and iodo-trihalomethanes are necessary. Recently Allard et al. developed a HS SPME-GC/MS method for simultaneous analysis of 10 THMs (4 regulated, chlorinated and brominated compounds and 6 unregulated iodinated ones) with detection limits ranging from 1 ng L^{-1} for iodoform to 20 ng L^{-1} for chloroform [50].

In this work a new analytical method for the simultaneous determination of the ten trihalomethanes present drinking water based on supported liquid hollow fiber membrane microextraction (HF-LPME) and GC-μECD was developed. In addition confirmation of compounds in the samples was performed by GC–MS. A remarkable advantage of this chromatographic approach is the combination of the sensitivity of electron capture detector with the selectivity of the mass spectrometer to get low detection limits and unequivocal identification of the analytes. The developed method is simple, reproducible and cheap, reaching low detection limits that makes the approach suitable for routine laboratories control in water distribution systems.

2. Experimental. Materials and methods

2.1. Chemicals and solutions

All reagents used were of highest purity, iodoform (CHI_3), 1,2 dibromopropane (used as internal standard SI) and THMs mixture 100 μg μL^{-1} of each compound: chloroform ($CHCl_3$), bromodicloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$), were purchased from Sigma-Aldrich (Steinhein Germany). Iodo-trihalomethanes (I-THMs): bromodiiodomethane ($CHBrI_2$ 90%), bromochloroiodomethane (CHBrClI 95%), chlorodiiodomethane ($CHClI_2$ 95%), dibromoiodomethane ($CHBr_2I$ 95%) and dichloroiodomethane ($CHCl_2I$ 95%) were purchased from Orchid Cellmark (New Westminster, BC, Canada). Methanol, *n*-hexane, toluene, acetonitrile and acetone were purchased from Teknokroma (Barcelona, Spain). *n*-Octanol was supplied from Merck (Barcelona, Spain).

Accurel Q 3/2 polypropylene hollow fiber membranes with an inner diameter of 600 μm, 200 μm of wall thickness and 0.2 μm pore size was obtained from Wuppertal (Germany). Ultrapure water (18 MΩ cm) was obtained from a Milli-Q water-purification system (Millipore, Watford, UK) and was used for spiked samples and blanks preparation.

Standard stock, intermediate and work solutions of each regulated THMs (chloroform, bromodicloromethane, dibromochloromethane and bromoform) were prepared in methanol at 20 mg L^{-1}, 200 μg L^{-1} and 5 μg L^{-1}, respectively. Standard stock, intermediate and work solutions of each I-THMs (iodoform, bromodiiodomethane, bromochloroiodomethane, chlorodiiodomethane, dibromoiodomethane and dichloroiodomethane) were prepared in methanol at 10 mg L^{-1}, 10 μg L^{-1} and 1 μg L^{-1}, respectively. Stock and intermediate solutions were stored into the dark at −20 °C for a maximum of one month. Work standard solutions were prepared daily in ultra pure water. The internal standard (IS) solution (1,2-dibromopropane) was prepared in methanol at a concentration of 5 mg L^{-1} to achieve a final concentration of 5 μg L^{-1}.

2.2. Sample collection

Water samples were taken in twelve sampling points from seven different water distribution systems. The sampling points were defined in finished water reservoirs of six water treatment plants (S1, S2, S3, S4, S5 and S6), in two water reservoirs of underground origin and disinfection treatment (S7 and S8), and four water reservoirs of the corresponding distribution systems (S2.1, S3.1, S3.2 and S4.1).

Water samples include five finished water from WTPs with conventional treatment: Aljaraque (S1), Lepe (S2), Riotinto (S4), Encinasola (S5) and Cumbres San Bartolomé (S6), one sample of finished water from Lepe WTP with advanced treatment (S3), two treated water from underground origen with disinfection treatment: Jabugo (S7) and Hinojales (S8) reservoirs, and four samples water from reservoirs of corresponding distribution systems: Ayamonte (S2.1 and S3.1), Isla Canela (S3.2) and Fuente la Corcha (S4.1). Sampling program with the characteristics of the water distribution systems and sample points are shown in Fig. S1 and Table S1 in the Supplementary information.

Samples were collected from the tap of each sample point. Before collecting tap water samples, the tap was opened for 5 min to assure the representativeness of the sample. The samples were collected into 125 mL amber glass bottles with teflon-lined screw caps,