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Fast analysis of volatile organic compounds and disinfection by-products in drinking water using solid-phase microextraction–gas chromatography/time-of-flight mass spectrometry

Vadoud H. Niri, Leslie Bragg, Janusz Pawliszyn*

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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ABSTRACT

A fast method was developed for the extraction and analysis of volatile organic compounds, including disinfection by-products (DBPs), with headspace solid-phase microextraction (HS-SPME) and gas chromatography/mass spectrometry (GC/MS) techniques. A GC/time-of-flight (TOF)–MS instrument, which had fast acquisition rates and powerful deconvolution software, was used. Under optimum conditions total runtime was 45 s. Volatile organic compounds (VOCs), including purgeable A and B compounds (listed in US Environmental Protection Agency method 624), were identified in standard water samples. Extraction times were 1 min for more volatile compounds and 2 min for less volatile compounds. The method was applied to the analysis of water samples treated under different disinfection processes and the results were compared with those from a liquid–liquid extraction method.

1. Introduction

Contamination of natural water resources is a growing problem worldwide, which leads to increased health problems and lack of safe drinking water. It is important not only to protect water resources from contamination, but also to monitor the levels of contaminants to ensure that water is safe to drink. Water is expected to contain trace amounts of some contaminants but this does not mean that the water constitutes a health risk [1]. The US Environmental Protection Agency (EPA) has many primary and secondary standards for drinking water to protect public health by ensuring safe drinking water and protected groundwater [2]. The term maximum contaminant level (MCL) is used by EPA, which is the highest level of a contaminant that is allowed in drinking water. Canada has similar guidelines, published by Health Canada, called The Guidelines for Canadian Drinking Water Quality, where the maximum acceptable concentrations (MAC) for contaminants are published [3].

Volatile organic compounds (VOCs) are common contaminants in drinking water. Some common VOCs are BTEX (benzene, toluene, ethylbenzene, and xylenes), chlorinated benzenes, dichloromethane (DCM), chloroethene (vinyl chloride), di- and trichloroethanes, dichloropropane, di- and trichloroethylenes, tetrachloroethylene, and carbon tetrachloride. Possible sources of these compounds include industrial effluent and waste disposal, solvents, gasoline or oil spills on the ground surface, pesticides and herbicides used in agriculture, and disinfection processes [1]. Disinfection by-products (DBPs) are formed during the disinfection process by the reaction of disinfectants with naturally occurring organic matter in source water. Depending on what kind of disinfectant is used, different types of by-products are produced. For example, chemical disinfection using chlorine, chloramines, or chlorine dioxide commonly produces trihalomethanes (THMs), haloacetic acids (HAAs), halogenated acetonitriles, chlorinated ketones, chlorinated furanones and cyanogen halides [4,5]. During ozonation, naturally occurring bromide in a water sample can react with ozone to form bromate [6]. The use of UV disinfection, at either low (LPUV) or medium pressure (MPUV), is increasing due to its advantages with respect to microbial inactivation and by-product formation [7]. Several potential toxicants, however, have been identified in photooxidised water, including oxalic and formic acids [8] and low molecular weight ketoacids and aldehydes [9]. Using UV light together with hydrogen peroxide (UV/H_2O_2), a process known as advanced oxidation process (AOP), can reduce DPBs formation [10].

Many different methods can be used to determine concentrations of contaminants in drinking water. Since the MCLs for many contaminants are very low (sub ng/ml), very sensitive analytical methods are highly demanded. Moreover, fast analytical methods are required because the number of samples to be analyzed is usually high. Gas chromatography/mass spectrometry (GC/MS) is considered one of the most promising techniques for water analysis regarding its high sensitivity for VOCs. However, the application of this technique is limited due to the time-consuming GC run

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* Corresponding author. Tel.: +1 519 888 4641.
E-mail address: janusz@uwaterloo.ca (J. Pawliszyn).

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times and sample preparation procedures. Therefore, development of fast GC methods coupled to rapid sample preparation techniques is invaluable in application of GC/MS in water analysis.

Solid-phase microextraction (SPME) is a simple, inexpensive, solvent-free extraction technique frequently used in water analysis [11–15]. This technique offers a unique combination of sampling and sample introduction to the chromatographic system by means of a single simple device. Previously, in order to achieve a fast GC, a dedicated injector has been used to reduce the injection band width in an isothermal GC [16,17]. Another time-consuming step in water analysis is pipetting samples into vials. The samples are usually collected in bottles on-site, transferred to the lab, and the pipetted into vials before analysis. Pipetting is not only time-consuming; if some of the target analytes are volatile, they may be lost during sample transfer. We have previously showed [18] that in order to eliminate pipetting, an approximate volume of sample can be collected separately in individual vials on-site, capped, transferred to the lab, and analyzed without any pipetting. Exact sample volumes of the samples can be obtained during analysis using volumetric standard [18].

In this study, a rapid method for extracting and analyzing volatile organic compounds, including disinfection by-products, was developed using SPME and GC/TOF–MS with a split/splitless injector. After selection of the best fiber, the amount of salt to be added, extraction temperature, and, extraction, incubation, and desorption times were optimized. A GC/TOF–MS instrument with rapid acquisition rates and powerful deconvolution software was used. The applicability of the method for the analysis of common VOC water contaminants was evaluated. The method was also applied in the analysis of water samples from different areas, which had undergone various disinfection processes.

2. Experimental

2.1. Materials and standard solutions

Stock solutions of Purgeables A (trichlorofluoromethane, 1,1-dichloroethene, dichloromethane, 1,1-dichloroethane, trichloromethane, tetrachloromethane, trichlorethene, 1,2-dichloropropane, 2-chloroethyl vinyl ether, 1,1,2-trichloroethane, tetrachloroethene, dibromochloromethane, chlorobenzene; 2000 μg/ml of each standard in methanol) and Purgeables B (benzene, *cis*-1,3-dichloropropene, bromodichloromethane, trans 1,3-dichloropropene, bromoform, ethylbenzene, 1,3-dichlorobenzene, 1,1,2,2-tetrachloroethane, 1,4-dichlorobenzene, 1,1,1-trichloroethane, 1,2-dichloroethane, toluene, *trans*-1,2-dichloroethylene; 2000 μg/ml of each standard in methanol) were purchased from Supelco (Bellefonte, PA, USA). A 1000 μg/ml standard solution containing Purgeables A and B was prepared by mixing an equal volume of the above standards. From this solution, a 500 μg/ml solution was prepared by diluting the last solution in methanol.

Salt solutions of 1%, 3%, 5%, 10%, 15%, 25%, and ∼35% (saturated) NaCl were prepared for salt percentage optimization experiments. NaCl was purchased from EMD Chemical (Gibbstown, NJ, USA). Standard solutions were prepared by spiking 1 μl of 500 μg/ml standard solutions into 5 ml of the salt solution for headspace extraction. The vials were capped immediately after spiking. The final concentration was 100 ng/ml. SPME fibers with different coatings, including polydimethylsiloxane (PDMS) (7 μm and 100 μm), Carboxen/polydimethylsiloxane (CAR/PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), and DVB/CAR/PDMS, were purchased from Supelco. All gases were supplied by Praxair (Kitchener, Canada) and were of ultra high purity.

2.2. GC/MS analysis

Gas chromatography was performed on both a Varian (Mississauga, Canada) 3800 gas chromatograph coupled with a Saturn 4000 ion trap-MS system, and an Agilent 6890 GC (Wilmington, DE, USA) with a Leco Pegasus III TOF MS (St Joseph, MI, USA). The latter has high sensitivity, fast acquisition rates and powerful deconvolution software. Automated analysis was performed with a CTC CombiPal autosampler from Leap Technologies (Carrboro, NC, USA) using the associated Cycle Composer software (Version 1.4.0). The PAL was equipped with a SPME fiber holder, a temperature-controlled six-vial agitator tray, two 32-vial sample trays, and a fiber conditioning device.

Separation was performed using a 30 m × 0.25 mm, 0.25 μm RTX-5 amine column from Restek (Bellefonte, PA, USA) on the Varian instrument and using 10 m × 0.18 mm, 0.18 μm RTX-5MS fused silica column on the Agilent instrument. In the optimized method for fast analysis using the Varian instrument, the column was initially set at 35 °C, ramped at 20 °C/min to 50 °C, then at 30 °C/min to 70 °C. Temperature was held at 70 °C for 1 min, then ramped at 30 °C/min to 150 °C, and held at this temperature for 0.87 min, giving a total run time of 6.00 min. For the Agilent/Leco instrument, the column was initially set at 70 °C, and then ramped at 70 °C/min to 100 °C for a total run time of 45 s. The peaks were fully separated on the Varian instrument within the 6 min run time. Although the

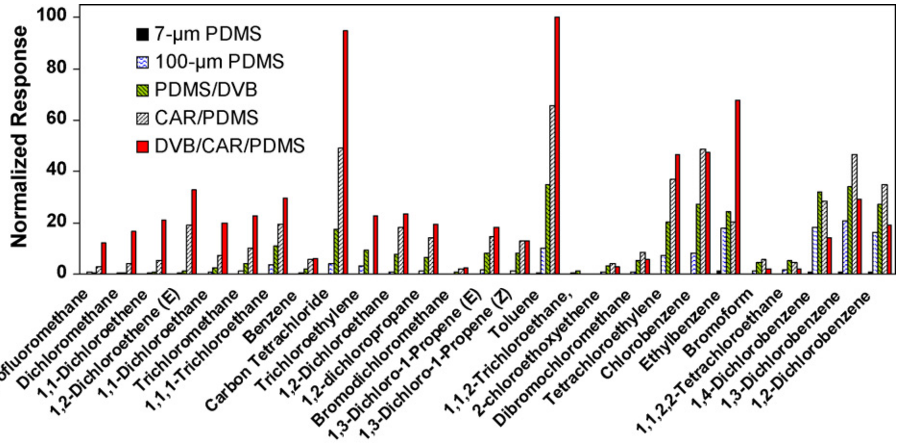

Fig. 1. Effect of coating type of fiber on extraction of VOCs.