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Single-drop microextraction with in-microvial derivatization for the determination of haloacetic acids in water sample by gas chromatography–mass spectrometry

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ABSTRACT

A new approach using single-drop microextraction (SDME) and gas chromatography–mass spectrometry for the determination of six haloacetic acids (HAAs) in water samples was presented. *n*-Octanol was used as extractant and derivatization reagent. HAAs were derivatized both simultaneously during the extraction in the solvent microdrop, and after extraction, inside a glass microvial (1.1 mm I.D.). Trifluoroacetic anhydride (TFAA) was used as the reaction catalyst. The influence of catalyst amount, derivatization time and temperature on the yield of the in-microvial derivatization was investigated. Derivatization reaction was performed using 1.2 μL of TFAA at 100 °C for 20 min. Extraction was performed using 1.8 μL of *n*-octanol containing TFAA (10%, v/v). Experimental parameters, such as, exposure time, sample pH and extraction temperature were controlled and optimized. Analytical parameters such as linearity, precision and limit of detection were also evaluated. The proposed method was proved to be a suitable analytical procedure for HAAs in water with limits of detection 0.1–1.2 μg/L. The relative recoveries range from 82.5 to 97.6% for all the target analytes. Precision values were from 5.1 to 8.5% (as intra-day relative standard deviation, RSD) and 8.8–12.3% (as inter-day RSD).

1. Introduction

Haloacetic acids (HAAs) are found in industrial wastes and as byproducts of water chlorination [1,2]. They are also found in other fields such as drugs, dyes and chemicals [3]. They are highly soluble in water and toxic to humans [4], animals [5], plants and algae [6].

The US Environmental Protection Agency (EPA) has set a maximum contaminant level (MCL) of 0.060 mg/L for the sum of concentrations of five haloacetic acids (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid and dibromoacetic acid) in water [7]. Qualitative target levels for HAAs have also been set by the World Health Organization (WHO): 50 mg/L for dichloroacetic acid and 100 mg/L for trichloroacetic acid [8].

Currently, methods used to determine HAAs involve gas chromatography (GC) with electron-capture detection (ECD) [9–12] or with mass spectrometry (MS) [13], capillary electrophoresis [14,15], liquid chromatography [16,17], electrospray ionization mass spectrometry (ESI-MS) [18], and ion chromatography [19,20]. Combination of high field asymmetric waveform ion mobility spectrometry (FAIMS) with ESI-MS has also been used to directly analyze nine HAAs at ppt levels in methanol and water solutions [18,21]. However, this method requires highly specialized FAIMS equipment not commonly available. Among these techniques, GC is the most widely used method due to its inherent advantages of high resolution, rapid separation, low cost and easy linkage with sensitive and selective detectors [9–13,22–24]. For the analysis of HAAs by GC, a prior derivatization step is necessary because of their low volatility and high polarity. After an extraction step, the derivatization of HAAs to short-chain esters using different reagents, such as diazomethane [9], acid–alcohol [13,14,22], dimethylsulphate [23] or BF_3–methanol [24], is performed. In EPA methods 552.1, 552.2, 552.3 and standard method 6251B [9–12], HAAs are extracted from water samples using methyl *tert*-butyl ether (MTBE) or anion exchange resins, converted into methyl esters using diazomethane or acidic methanol, and determined using GC-ECD. The overall sample preparation is lengthy and complicated (3 h for method 552.2), and the GC run time is approximately 50 min. In 2003, Jia et al. used pentafluorobenzyl bromide (PFBBr) as a new and suitable reagent for derivatization of nine HAAs [25]. PFBBr is a widely used reagent for derivatization of different compounds [26,27]. The reaction between HAAs and PFBBr was performed in 20 mg/mL PFBBr solution containing K_2CO_3. The reaction time was approximately 2.5 h. GC–MS was used to identify the reaction products. The reaction pathway is illustrated in Fig. 1 [25].

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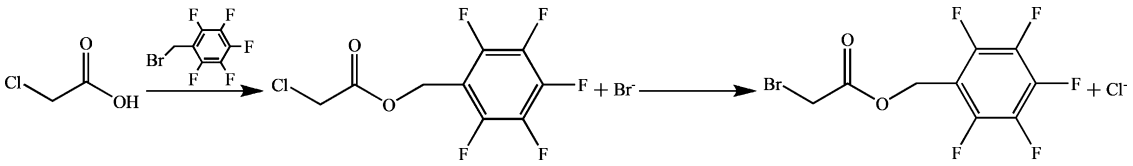

Fig. 1. Derivatization reaction of HAAs with PFBBr [25].

Conventional extraction methods such as liquid–liquid extraction (LLE), derivatization, and separation steps are labor-intensive, time-consuming, and involve reagents that are toxic and carcinogenic. A few studies on solid-phase extraction (SPE) [28,29] and solid-phase microextraction (SPME) [13,23,30] for analysis of HAAs have also been reported. Hollow fiber supported liquid membrane extraction (SLME) followed by on-line HPLC–UV detection was also used as an alternative sample preparation technique for the determination of HAAs [31,32]. The SLME method has several advantages, such as simple instrumentation, requiring small solvent volumes and offering high enrichment factors.

In recent years, single-drop microextraction (SDME) and liquid-phase microextraction (LPME) techniques have been developed as an alternative to SPME [33,34]. In these methods, analytes are extracted in a few microliters of a solvent. SDME avoids some problems of the SPME method such as sample carry-over and fiber degradation; it is also fast, inexpensive and uses very simple equipment. However, use of a few microliters of the extraction solvent makes derivatization of extracted compounds difficult. Therefore, to derivatizing analytes after SDME, in-syringe and in-microvial derivatization have been developed [35–38].

Recently, hollow fiber membrane liquid-phase microextraction (HF-LPME), direct derivatization and GC-ECD have been applied for analysis of HAAs in water samples [39]. The method has improved the sample preparation step of the EPA method 552.2 by combining the derivatization and the extraction into one step prior to determination by GC-ECD. The HAAs were derivatized with acidic methanol into their methyl esters and simultaneously extracted with supported liquid hollow fiber membrane in headspace mode.

To our knowledge, this paper is the first to report the determination of HAAs in water samples using SDME. In addition, derivatization of HAAs with bisTMSA and/or *n*-octanol followed by GC determination has not been reported previously. The first aim of this work was to evaluate three derivatization reagents including bisTMSA, PFBBr and *n*-octanol for the derivatization of HAAs. The second aim of this research was to develop a new method based on single drop microextraction and in-microvial derivatization followed by GC–MS for the determination of six HAAs (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid and bromochloroacetic acid) in water. *n*-Octanol was used both as extracting solvent and derivatization reagent. Derivatization of HAAs was performed both simultaneously during the extraction in the solvent microdrop and after extraction in a glass microvial. Trifluoroacetic anhydride (TFAA) was used as the reaction catalyst. Parameters that affect the derivatization reaction yield and the extraction efficiency of the SDME method were studied and optimized. The analytical performances and possible applications of the method in real sample analysis were also investigated.

2. Experimental

2.1. Chemicals and reagents

A standard mixture of six haloacetic acids containing monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA) at a concentration of 2000 mg/L in methyl *tert*-butyl ether was purchased from Supelco (Bellefonte, PA, USA). An intermediary standard solution at a concentration of 200 mg/L was prepared by diluting the standard solution in acetone. More diluted working solutions were prepared daily by diluting the intermediary standard solution with triple distilled water. Water samples were prepared by spiking triple distilled water with analytes at known concentrations to study the extraction performance under different conditions. The stock solution of internal standard (I.S.) was prepared by dissolving 15.5 mg of 1-bromonaphthalene in 10 mL hexane.

Stock solutions of MCAA, DCAA and TCAA (1000 mg/L) were prepared by dissolving the corresponding mass of solid compounds in acetone. These solutions were used for derivatization with PFBBr.

HPLC-grade hexane, toluene and acetone were purchased from Caledon Laboratories (Georgetown, Ont., Canada). TFAA was obtained from Merck (Darmstadt, Germany). GC grade *n*-octanol and PFBBr were obtained from Fluka (Buchs, Switzerland). GC grade *N*,*O*-bis(trimethyl silyl)acetamide (bisTMSA) was purchased from Merck. The water samples were acidified with concentrated sulphuric acid (95–98%, Merck). Other reagents were purchased from Merck.

2.2. Instrumentation

Gas chromatographic analysis was carried out using a Fisons Instrument (Rodano, Italy) model 8060 fitted with a split/splitless injector and a Trio 1000 mass spectrometer (Fisons Instruments, Manchester, England) detector. Helium (99.999%) at a head pressure of 50 kPa was used as carrier gas. The components were separated on a 30 m × 0.25 mm I.D., 0.25 μm film thickness Rtx-5MS column (Restek, Bellefonte, PA, USA). The split/splitless injector temperature was set at 240 °C. The column was initially maintained at 80 °C for 1 min; subsequently, the temperature was increased to 180 °C at a rate of 25 °C/min (11 min hold) then was increased to 250 °C (30 °C/min, 2 min hold). The GC–MS interface and the ion source temperatures were set at 200 °C. In the optimization studies, the mass spectra were acquired as full scans from *m*/*z* 30 to 310 (2 scans/s) under a 70-eV ionization potential. In order to increase sensitivity, quantitative analysis was performed in time scheduled selective-ion monitoring (SIM) mode. Table 1 lists the analytical SIM conditions for the determination of studied compounds.

Table 1
Retention times, selected ions and time windows of *n*-octyl derivatives of haloacetic acids.

Compound	Retention time (min)	Selected ions (*m*/*z*)	Time window (min)
MCAA	6.87	79, 95	6.1–7.2
DCAA	7.35	48, 76	7.2–7.5
MBAA	7.4	121, 123, 139	7.2–7.5
IS	7.66	127, 208	7.5–7.8
TCAA	7.9	36, 110, 121	7.8–8.05
BCAA	8.1	127, 129, 131	8.05–8.4
DBAA	9.2	120, 122, 173	8.6–9.6