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Continuous, on-line monitoring of haloacetic acids via membrane extraction

Xiaoyan Wang, Dawen Kou[1], Somenath Mitra*

Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ 07102, USA

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Abstract

Haloacetic acids are an important class of disinfection byproducts that are being regulated. In this paper we report novel instrumentation for continuous monitoring of the nine haloacetic acids. Hollow fiber liquid–liquid membrane extraction (LLME) and supported liquid membrane extraction (SLME) followed by on-line HPLC-UV detection were studied. With continuous LLME, seven halo-acetic acids could be analyzed and enrichment factor (EF) was around 50. All the nine acids could be extracted and quantified by continuous SLME. Experiments with laboratory standards demonstrated that EF and extraction efficiency could be as high as 500 and 54%, respectively. Relative standard deviations based on seven replicates were between 3.3 and 10.3%, and the MDLs were at sub-ppb levels.

Keywords: Supported liquid membrane extraction; Membrane extraction; Haloacetic acids; Water monitoring; Disinfection byproducts

1. Introduction

Chlorination is one of the most common methods for disinfecting drinking water [1]. Chlorine reacts with naturally occurring acids to form halogenated disinfection byproducts (DBPs), some of which are known carcinogens. Trihalomethanes (THMs) and haloacetic acids (HAAs) are the major volatile and nonvolatile DBPs [2]. The names, abbreviations, pK_a values and octanol–water partition coefficients (log P) of the nine HAAS are included in Table 1. USEPA has classified DCAA as a probable human carcinogen and TCAA as a possible human carcinogen. Furthermore, decarboxylation of HAAs results in the formation of THMs, which are also carcinogens [3]. USEPA has regulated the total maximum contaminant level (MCL) in drinking water of the five HAAs: MCAA, MBAA, DCAA, BCAA, and DBAA to be less than 60 μg/L [4].

Currently there are several USEPA approved methods for HAAs analysis (EPA method 552.1, 552.2 and 6251) [5–6]. All these methods involve cumbersome liquid–liquid extraction or ion exchange and derivatization, followed by GC-ECD detection. They have several limitations, for example, EPA method 552.1 uses ion exchange and derivatization followed by GC-ECD detection. It consumes less solvent, however the interference from anions increases the detection limits [5], and it can only determine six of the HAAs. Typical analysis time for the above methods varies between three to four hours. Alternative methods that do not need the derivatization prior to analysis have been developed based on, liquid chromatography (LC) [7–8], ion chromatography (IC) [9–14], capillary electrophoresis (CE) [15], and electrospray ionization high-field asymmetric waveform ion mobility spectrometry and mass spectrometry (ESI-FAIMS–MS) [16]. ESI-FAIMS–MS provides low detection limit, has excellent sensitivity and selectivity, but the high cost limits its availability. The detection limits of the LC, IC and CE methods are higher than the GC methods. Many of the alternative methods have been used for five or six HAAs, and only a few are applicable for all the nine HAAs.

* Corresponding author. Tel.: +1 973 5965611; fax: +1 973 5963586.
E-mail address: mitra@njit.edu (S. Mitra).
[1] Present address: Hoffmann-La Roche Inc., Pharmaceutical and Analytical R&D, 340 Kingsland St., Nutley, NJ 07110, USA.

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Table 1
Analytical performance of continuous SLME-HPLC

Names	Abbreviation	log P[a]	pK_a[a]	RSD[b] (%)	EF	EE (%)	MDL[c] (ng/mL)
Monochloroacetic acid	MCAA	0.22	2.87	10.3	71.3	8.9	6.84
Dichloroacetic acid	DCAA	0.92	1.26	10.3	335.5	41.9	0.32
Monobromoacetic acid	MBAA	0.41	2.89	3.5	335.9	42.0	0.33
Bromochloroacetic acid	BCAA	1.14	1.39	4.2	273.6	34.2	0.13
Dibromoacetic acid	DBAA	1.69	1.47	4.8	412.1	51.5	0.15
Trichloroacetic acid	TCAA	1.33	0.51	5.7	383.4	48.0	0.18
Bromodichloroacetic acid	BDCAA	2.31	1.09	5.9	412.3	51.5	0.18
Chlorodibromoacetic acid	CDBAA	2.91	1.09	3.3	428.4	53.6	0.10
Tribromoacetic acid	TBAA	3.46	3.13	8.8	305.5	38.2	0.28

[a] log P and pK_a values are from Ref. [30].
[b] Relative standard deviations (RSD) based on seven replications were obtained with continuous SLME, the water containing 21 ppb MCAA, 3 ppb MBAA, and 1 ppb rest 7 HAAs flowed at 4 mL/min and the acceptor at 0.005 mL/min.
[c] The method detection limits (MDLs) were obtained following a standard EPA procedure [31].

Despite these recent developments, currently there is no method for continuous, on-line monitoring of all the nine HAAs. Automated on-line measurements are less expensive, provide real-time information and have better accuracy and precision [17]. Since there is less manual sample handling, these techniques tend to be less prone to contamination. The goal of this study is to develop automated, on-line methods for the continuous monitoring of all the nine HAAs in water.

Membrane extraction has recently emerged as a promising technique for sample enrichment. It has several advantages, such as simple instrumentation, requiring small solvent volumes and offering high enrichment factors. It allows continuous on-line extraction in a flow system, and can be coupled to a GC [18–22], HPLC [23–25], mass spectrometry (MS) [26] and CE [27] for continuous on-line monitoring.

There are two major approaches of membrane extraction, supported liquid membrane extraction (SLME) and liquid–liquid membrane extraction (LLME) [28]. SLME is a three-phase extraction system, where the analytes are extracted from an aqueous sample into an acceptor via an organic extractant held in the pores of the membrane. It works well for the extraction of highly polar and ionizable compounds [29]. Recently, we have reported supported liquid membrane micro-extraction (SLMME) for the extraction of HAAs from water [30]. This technique provides high enrichment and relatively short analysis time. LLME is a two-phase system, where the analytes are extracted from an aqueous sample into an organic acceptor. Here, the organic solvent contacts the water sample across the membrane without direct mixing. Another advantage of the membrane interface is that there is no emulsion formation, which is a common occurrence in conventional liquid–liquid extraction.

The objective of this study is to develop membrane extraction technique for continuous on-line monitoring of HAAs. Both continuous LLME and SLME followed by HPLC-UV detection were investigated in this research.

2. Experimental

The instrumentation used for SLME and LLME were quite similar and is shown in Fig. 1. It includes a hollow fiber membrane module, two pumps and a HPLC system. The first pump (a Hewlett-Packard 1050 HPLC pump) was used for the delivery of the acceptor, and the other (a Beckman 110B pump) for the donor. An automated six-port HPLC

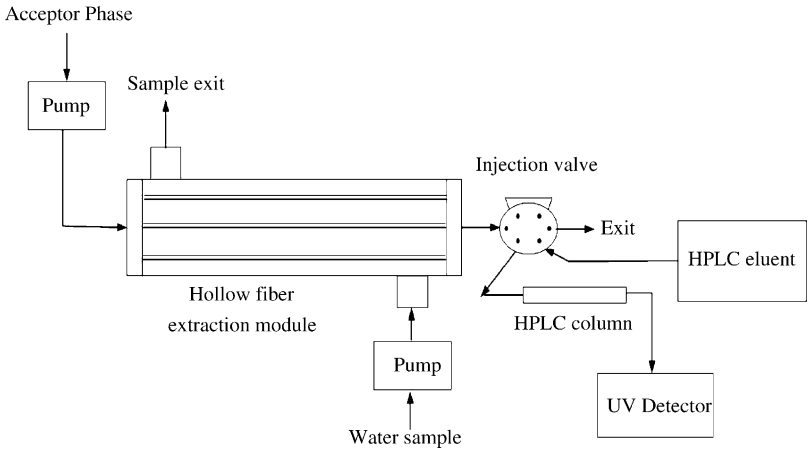

Fig. 1. Schematic diagram of continuous membrane extraction followed by HPLC-UV detection.