Report for 2002NJ4B: CONTINUOUS, ON-LINE MONITORING OF HALOACETIC ACIDS IN WATER USING ANALYTICAL MEMBRANE EXTRACTION

- Book Chapters:
  - Kou, Dawen; Somenath Mitra, 2003, Extraction of Semi-volatile Organic Compounds from Solid Matrices, in S. Mitra (ed), Sample Preparation Techniques in Analytical Chemistry, New York: John Wiley & Sons, In print.
  - Slack, Gregory; Nicholas Snow, and Dawen Kou, 2003, Extraction of Volatile Organic Compounds from Solids and Liquids, in S. Mitra (ed) Sample Preparation Techniques in Analytical Chemistry, New York: John Wiley & Sons, In print.
- Conference Proceedings:
  - Wang, Xiaoyan; Dawen Kou, Edmund J. Bishop, and Somenath Mitra, 2003, Supported Liquid Membrane Micro-Extraction (SLMME) for the Determination of Trace Organic Acids, presented at the 27th International Symposium on Capillary Chromatography, Las Vegas, NV.
- Articles in Refereed Scientific Journals:
  - Kou, Dawen; Xiaoyan Wang, and Somenath Mitra, 2003, Supported Liquid Membrane Micro-Extraction (SLMME) with HPLC Detection for Monitoring Trace Haloacetic Acids in Water, Analytical Chemistry, In Review.
- Dissertations:
  - Kou, Dawen; 2002, Development of Membrane Extraction Techniques for Water Quality Analysis, Ph.D. Dissertation, Department of Chemistry and Environmental Science, College of Science and Liberal Arts, New Jersey Institute of Technology, Newark, NJ, 91 pages.

Report Follows:

Year 2002 Project Report to U.S. Geological Survey and NJWRRI

Continuous, On-Line Monitoring of Haloacetic Acids in Water Using Analytical Membrane Extraction

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Part II

Problem and Research Objectives:

Haloacetic acids (HAAs) are a group of compounds known as disinfection by-products (DBPs). They are generated during the disinfection (e.g. chlorination) of drinking water that contains natural organic matters (humic and fulvic compounds) and bromide (if present). The U.S. EPA lists nine HAAs (monochloroacetic acid, or MCAA, monobromoacetic acid, or MBAA, bromochloroacetic acid, or BCAA, dichloroacetic acid, or DCAA, dibromoacetic acid, or DBAA, bromodichloroacetic acid, or BDCAA, trichloroacetic acid, or TCAA, tribromoacetic acid, or TBAA, dibromochloroacetic acid, or DBCAA) as the major fraction of non-volatile DBPs. HAAs are toxic to humans, plants, and particularly to algae [1]. EPA has classified dichloroacetic acid and trichloroacetic acid as suspected carcinogens. According to EPA's regulations pertaining to disinfectants and disinfection by-products (D/DBP) [2], the current Maximum Contamination Level (MCL) for total HAAs in drinking water is 60 μg/L.

The importance of HAAs calls for sensitive methods for their determination. The standard EPA method 552 [3] for HAA analysis involves liquid-liquid extraction followed by derivatization and GC (gas chromatography) analysis. Low detection limits are attained at the cost of a lengthy, cumbersome extraction-derivatization procedure. In light of the limitations of the EPA methods, considerable efforts have gone into developing alternative techniques that do not require derivatization. These alternatives include methods using LC (liquid chromatography, and ion chromatography) [4-5], CE (capillary electrophoresis) [6], and ESI-MS (electrospray ionization mass spectrometry) [7]. ESI-MS provides excellent sensitivity and selectivity, but limited availability of the instrument precludes its wide use. With the current sample preconcentration techniques, the LC and CE methods are not sensitive enough for the analysis of drinking water samples.

The objective of this study is to develop a novel method/technique for HAA monitoring with high selectivity and sensitivity. The method will not involve derivatization, and will be simple, easy to use, and minimize the use of toxic solvents in sample preparation. It will be used to carry out continuous, on-line monitoring of haloacetic acids in drinking water.

Methodology:

A supported liquid membrane microextration (SLMME) technique was developed for the extraction and preconcentration of HAAs in water. Figure 1 illustrates the concept of SLMME. The HAAs first diffused from the bulk donor solution to the surface of the membrane, and then partitioned into the membrane liquid. After migrating across the membrane, they were extracted into the acceptor via deprotonation. The two processes occurred simultaneously, so the extraction was highly efficient. The concentrations of the neutral compounds remained unchanged on both sides, which implied no enrichment. Basic compounds were in the charged form in the donor and were not extracted. Therefore, SLMME provided both high enrichment and high selectivity for the acidic compounds.

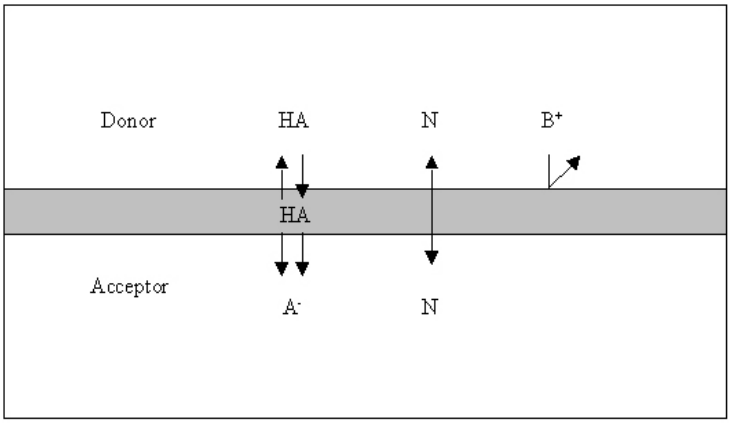

Figure 1. The concept of SLMME, HA, N and B^+ represent acids, neutral species, and bases respectively.

The SLM used in this study was made by impregnating a segment of microporous hollow fiber with a membrane liquid for a period of ten seconds. Two types of polypropylene microporous hollow fiber membranes were used to make the SLM. One was Celgard® X20. It had an i.d. of 400 μm and an o.d. of 460 μm, with an average pore size of 0.03μm and porosity of 40%. The other was Accurel® PP Q 3/2.

It had an i.d. of 600 μm and a wall thickness of 200μm, with an average pore size of 0.2 μm and porosity of 75%. The membrane liquids tested were di (2-ethylhexyl) phosphate (DEHPA) and di-hexyl ether (DHE). The effect of adding trioctylphosphine oxide (TOPO) into DHE was also investigated. The optimum combination was found to be 12cm PP Q3/2 membrane with DHE containing 5% TOPO as the supported membrane liquid.

A HPLC method that is capable of separating all nine HAAs has been developed. A Hewlett-Packard 1050 HPLC system was used for the analysis, with a Waters Resolve® C18 column. A Waters 486 Tunable Absorbance UV Detector was used at the wavelength of 210nm. The HPLC eluent was a 0.4M ammonium sulfate solution. The flow rate was programmed as follows. It was held constant at 0.5 mL/min during the first five minutes, and then increased gradually to 2.0 mL/min in the next three minutes. From 8 to 13 minute, the flow rate was kept constant at 2.0 mL/min. The injection volume was 20μl. Minichrom V. 1.62 software was used for data acquisition and analysis.

Principal Findings and Significance:

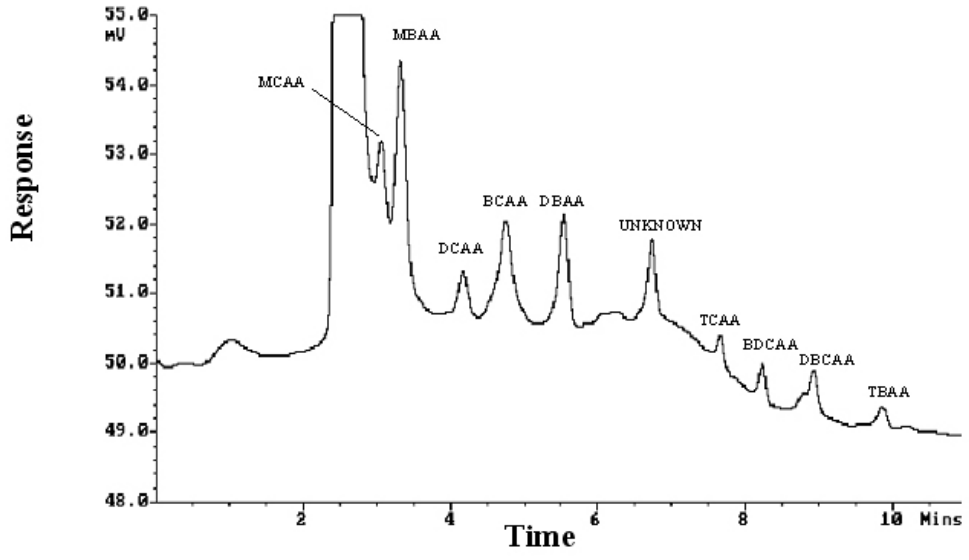

Figure 2. The chromatogram of nine HAAs in reagent water after SLMME. The concentrations were: MCAA at 40ppb, MBAA at 10ppb, DCAA at 0.8ppb, and the other six HAAs at 0.4ppb.

The developed supported liquid membrane microextraction technique is capable of achieving up to 3000 fold of enrichment of HAAs from water. The developed HPLC method using flow programming can separate the HAAs in 10 minutes. The extract from SLMME can be directed analyzed by this HPLC method, without derivatization. Figure 2 shows a chromatogram of HAAs at ppb level obtained using the developed SLMME-HPLC method. The analytical performance of this method is summarized in Table 1. This method showed excellent precision, and the detection limits were lower than or comparable to those by the standard EPA method. The SLMME device is inexpensive, easy to make, and uses only a few microliters of organic extractant. Work is in progress on coupling SLMME on-line with HPLC for real-time monitoring.

Table 1. Analytical Performance of SLMME-HPLC

	MDL (μg/L or ppb)*	MDL by EPA Method 552.2 (μg/L or ppb)*	Linear Dynamic Range (μg/L)	Linear Regression Coefficient	RSD (%)**
MCAA	7.7	0.273	20-160	0.999	6.0
MBAA	2.0	0.204	10-80	0.998	6.9
DCAA	0.21	0.242	0.8-20	0.999	11.9
BCAA	0.09	0.251	0.4-20	0.999	6.6
DBAA	0.10	0.066	0.4-20	0.999	5.1
TCAA	0.05	0.079	0.4-20	0.999	2.6
BDCAA	0.13	0.091	0.4-20	0.999	7.1
DBCAA	0.12	0.468	0.4-20	0.999	5.7
TBAA	0.08	0.82	0.4-20	0.999	3.7

* The Method Detection Limit (MDL) was obtained following a standard EPA procedure [8].
** The Relative Standard Deviations (RSD) based on seven replications was obtained at concentrations of 40, 10, and 0.8ppb for MCAA, MBAA, and DCAA respectively, and the concentration was 0.4ppb for the rest of the HAAs.

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