Continuous On-Line Monitoring of Trihalomethanes in Chlorinated Drinking Water using an Automated System Based on Pulse Introduction Membrane Extraction and High Speed Gas Chromatography/Mass Spectrometry

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An automated system based on pulse sample introduction membrane extraction and gas chromatography/mass spectrometry (GC/MS) has been developed for on-line monitoring of Trihalomethanes (THMs) in chlorinated drinking water. Pulse samples were injected into the membrane through a sample loop. Zero air was used as the eluent to elute the water samples and also acted as the purging gas. The use of zero air as the purging gas facilitates the cleanup of the membrane to reduce the tailing part of sample input. Under typical operating conditions, the cycle time can be reduced to less than 4 min. The detection limits of this system were found to be about 50 ppt, 50 ppt, 50 ppt, and 20 ppt for $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$, respectively. The utility of this system was demonstrated with a ten-hour on-line monitoring of THMs in tap water.

INTRODUCTION

Conventional analytical techniques for measurement of volatile organic compounds in water are purge/trap, headspace and solid phase microextraction. These techniques usually involve distinctive steps, such as sampling at site, transportation to the laboratory and sample preparation before GC or GC/MS analysis and, therefore, are not suitable for continuous on line monitoring.

Membrane separation has emerged as an attractive alternative for interfacing an extraction step directly to a gas chromatograph[1-5] or to a mass spectrometer.[6-10] Membranes offer the advantage of continuous on-line extraction. The membrane is a selective barrier - it allows some analytes and prevents others from passing through the membrane wall to the analytical system.

In membrane introduction, the sample is either introduced continuously or as a pulse (flow injection). In continuous introduction, the water sample continuously flows through the feed side of the membrane and the organics are removed continuously on the permeated side with a stream of helium. Earlier, we have reported a system based on continuous introduction in combination with membrane extraction and fast GC/MS.[11] In the approach, the conventional 30 or 60 m capillary column was replaced with a 5 m short column for fast separation. The fast separation leads to the coupling of GC/MS with membrane without losing the characteristic of on-line monitoring. The cycle time was reduced to less than 5 minutes, and the utility of the system was demonstrated with the continuous on-line monitoring of THMs in tap water.

In continuous extraction, the analysis is based on the assumption that the measurement is made when the permeation has reached a steady state. In general, the column separation time is often longer than the time required to reach the steady state. Therefore, the frequency of analysis is limited by the separation time rather than the time to reach the steady state. However, in the analysis of THMs in water using the continuous membrane introduction fast GC/MS, [11] the time to reach the steady state is longer than the column separation time. Consequently, the signals of the GC/MS mass chromatograms may not represent the true concentration in the sample stream. The signals are also difficult to interpret because the time needed to reach steady state is not the same for four different THMs. In on-line monitoring, if there is a change of concentration in the sample stream, the signal of bromoform, the THM with the slowest permeation rate, will appear much later than the signal of chloroform.

The other sample introduction technique, the flow injection approach, has been used widely in membrane introduction mass spectrometry (MIMS)[5-10] and for interfacing membrane extraction with GC as well.[1-5] This technique has the advantage of analysis of individual small volume sam-

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ples. However, the memory effect is often serious and may result in carryover from one sample to the next.

An important consideration in membrane extraction is the slow permeation of the analytes through the boundary layer and the membrane. Analytes diffusing through the boundary layer and the membrane are the major resistance to mass transfer and are the rate limiting steps. It has been shown that the aqueous boundary layer is the major resistance to permeation when thin membrane is used.[12-14] Recently, a variation of flow injection technique, referred to as the pulse introduction,[15-16] has been proposed to reduce the memory effect. In pulse introduction, a sample pulse is introduced into an eluent stream that transports it into the membrane. However, unlike flow injection, a stream of the gas such as nitrogen is then introduced into the membrane to eliminate the aqueous boundary layer. The elimination of aqueous boundary layer results in higher extraction efficiency and less memory effect.

One goal of this laboratory is to develop automated systems for on-line and real time monitoring of environmental pollutants. Our earlier system for THMs monitoring has excellent sensitivity but suffers from serious memory effect. [11] The goal of this study is to establish an automated system with minimum memory effect but with enough sensitivity for on-line monitoring of THMs in drinking water.

EXPERIMENTAL SECTION

Chemicals and Reagents

The trihalomethane compounds of 98+% purity were purchased from Aldrich, Avocado, Chem-Service and Merck. Stock solutions were prepared by dissolving 100 mg of each individual compound in 10 mL methanol. Appropriate amounts of these stock solutions were spiked into 100 mL of reagent water to give different concentrations of THMs aqueous stock solutions. The standard solutions were prepared by serial dilution of the aqueous stock solution with reagent water. The toluene-d8 (from Aldrich) internal standard solution was prepared by dissolving pure standard in reagent water.

Apparatus and Procedure

The pulse sample introduction membrane extraction fast GC/MS system with zero air as eluting and purging gas is shown in Fig. 1. The instrument consisted of a laboratory built pulse introduction membrane extraction system, cryofocusing unit of a Takmer 6000 AERO Trap Desorber and a Fisons GC 8000/MD 800 GC/MS. The cryofocusing unit of a Takmer 6000 AERO Trap Desorber was used as the interface between the membrane extraction system and GC/MS. A 5 m DB-5MS (J&W Scientific, 0.250 mm ID, 0.25 μm film thickness) capillary column was used for separation and 9 cm of the column was mounted inside the cryofocusing unit as the trap tube. The column temperature was kept at 50 °C. The interface and ion source temperatures of GC/MS were set at 200 °C. The MS was operated at selected ion monitoring (SIM) mode (10 ms dwell time/ion). Four ions, 83, 98, 129, and 173 were monitored. The *m/z* 83 ion is the base peak of chloroform and bromodichloromethane. The *m/z* 98 ion is the base peak of the internal standard (toluene-d8). The *m/z* 129 and 173 ions are the base peaks of dibromochloromethane, and bromoform, respectively. The scan rate was 0.112 sec/cycle giving at least 8 data points per peak.

The membrane extraction system was constructed from a 4 cm piece of stainless tube (0.085 in. ID × 1/8 in OD) and two Swagelok T-unions (1/8 in.). A 8 cm Dow Corning silastic hollow fiber membrane (SILASTIC® Medical Grade Tubing, 0.025 in. ID × 0.047 in. OD, Dow Corning) was mounted inside the stainless tube. The exposed length of the hollow fiber membrane in the membrane introduction system was about 5 cm. The membrane extraction system is used so that the carrier gas flows over the outside of the membrane while the sample solution flows inside the membrane. During operation, a stream of zero air (eluent) flowed continuously through the membrane extraction system at a flow rate of 25 mL/min. An aqueous sample solution flowed continuously through the 0.5 mL sample loop of a six port valve by a peristaltic pump (Cole-Parmer). To avoid contamination of the peristaltic pump, the pump was located at the downstream of the flow system. The internal standard solution (toluene-d8) was pumped through a T-connector using a second peristaltic pump and mixed with the sample solution in the mixing coil (Teflon tubing 0.030 in. ID × 0.062 in. OD × 3 m). A continuous flow of helium, flow rate 1.6 mL/min, was supplied to the membrane introduction system. The helium served as a stripping gas as well as a carrier gas for GC/MS. The helium flow carries the components directly into the cryofocusing system before entering the GC/MS.

During sample injection, the six port valve was switched and the water sample in the loop was transported to the membrane by a stream of zero air. For on-line monitoring of THMs in water, periodically injections were made. Each injection sent a pulse of sample into the membrane module.

The system was designed to be an automated system. Each cycle was initiated by the Tekmar 6000 Desorber. A tart signal from the Tekmar 6000 Desorber was sent to the GC/MS to initiate the analysis. An event signal from the GC/MS was then sent to the electrical controlled six port

valve (Valco International) through a relay to switch the valve. The typical cycle time was less than 4 minutes.

The procedures of the analysis can be divided into three steps: membrane extraction, preconcentration and fast GC/MS. Aqueous solution in the sample loop was transported to the membrane module by zero air. The THMs were extracted from the sample solution by permeation across the membrane. In the preconcentration and focusing step, the cryotrapping tube was cooled to -165 ℃ by a continuous flow of liquid nitrogen, and the THMs were collected in the cryotrapping column from the sample/helium flow. To end sample collection, the temperature of the cryotrapping tube was quickly increased (about 500 °C/min) to the injection temperature (0 °C) , and then maintained at the injection temperature during the injection step (1 min). The THMs in the cryotrapping column were released into the separation column and detected by MS. After the injection step, the temperature of the cryotrapping column was increased to 200 °C at about 500 °C/min, and the system was ready for the next analysis.

RESULTS AND DISCUSSION

Continuous, on-line monitoring involves a series of injections. For each sample injected, the permeation must be completed before the next injection is made. To achieve continuous on-line monitoring, a short lag time is required so that each analysis can be quickly completed. In pulse introduction membrane extraction, either a gas or a liquid can be used as

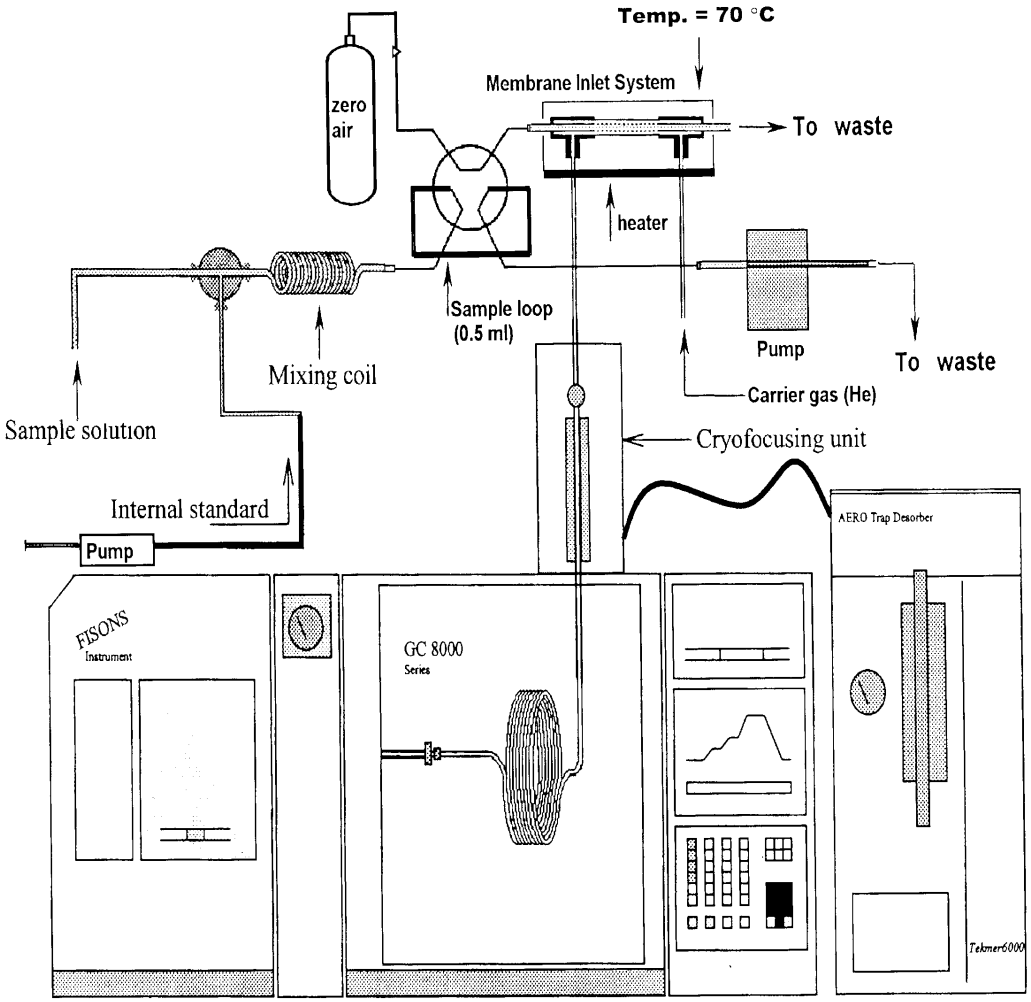

Fig. 1. Setup of the pulse sample introduction membrane extraction GC/MS system using zero air as the eluent and as the purging gas.

the eluent. Initial study was conducted using reagent water as the eluent. The results (data not shown) suggested that the lag time was too long to be suitable for high frequency sampling. We then switched to using gas (zero air) as the eluent. The zero air eluted the water sample when the sample solution was introduced into the membrane. The zero air was also used as the purging gas for purging the membrane to eliminate the aqueous boundary formed on the membrane surface and cleaning the membrane to eliminate the tailing part of sample input.

Injection volume is an important parameter to the sensitivity and the lag time. In general, a larger injection volume would increase sensitivity but at a cost of longer lag time. In this study, a 0.5 mL sample loop was chosen for sampling. In addition to the trade-off between sensitivity and lag time, the choice of a 0.5 mL injection volume is also based on the need to maintain a stable zero air flow rate. It was found that it is relatively difficult to maintain a stable zero air flow rate if the injection volume is larger than 0.5 mL. Even with a 0.5 mL aqueous sample, the flow rate dropped from 25 mL/min to 24 mL/min when a 0.5 mL water sample was transported to the membrane. The change of flow rate is mainly due to the compressibility of gas. The water sample presents a massive barrier for the gas to flow at a preset flow rate.

Under the conditions that 0.5 mL sample volume is selected, it is important to find a condition so that sensitivity and instrument response time can be optimized. It has been reported that permeation rate increases with temperature of the membrane.[17-18] Consequently, the lag time, which is the duration of the permeation, is reduced at higher membrane temperatures. The effect of membrane temperature to the sensitivity and the lag time is shown in Fig. 2. It can be seen that at the temperature of 25 °C, the signal of bromoform, the THMs of slowest permeation rate, is still significant after 25 minutes. However, when the temperature was increased from 25 °C to 70 °C, less than 5 % of signal was observed at the second cycle. In addition, not only the memory effect was significantly reduced, the intensities of the signals were also much higher than those at 25 °C (Fig. 2). Based on these results, a membrane temperature of 70 °C was chosen in this approach.

More analytes may permeate across the membrane at a temperature above 70 °C. A temperature higher than 70 °C was not suggested because the signals were found to be not quite reproducible at a temperature higher than 70 °C. Excess water molecules, which permeate across the membrane, are believed to be responsible for the deterioration of reproducibility. Even at a temperature much lower than 70 °C, such as 25 °C, the number of water molecules across the membrane is believed to be much higher than the analytes. Without removing the water molecules, the baseline rises slightly; the ionization efficiencies of dibromochloromethane and bromoform are also suppressed by water molecules. To overcome the problem, a strategy based on programmed temperature vaporization injection[11] was adopted in this approach. The temperature of the trap is maintained at 0 °C for a duration of one minute during injection. By doing that, the major-

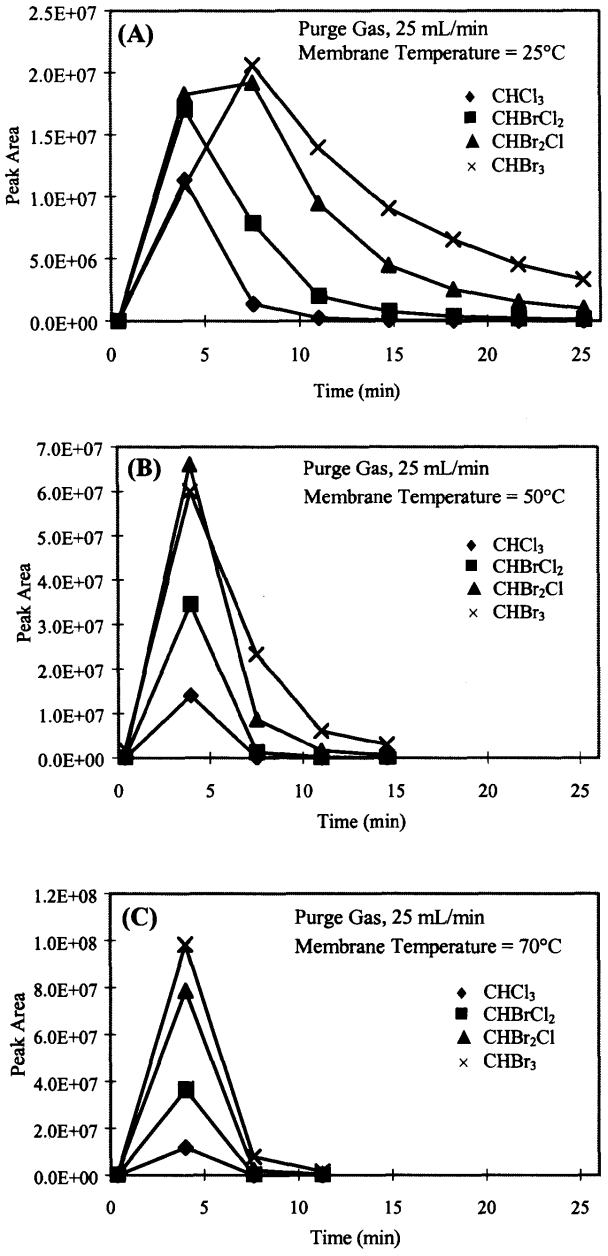

Fig. 2. The effect of membrane temperature to lag time and signal intensity.

ity of water molecules will remain in the trap during separation and ionization. After the injection step, water was desorbed to the column by ramping the injection temperature to 200 ℃. With programmed temperature vaporization injection, typical mass chromatograms of THMs and internal standard (toluene-d8) obtained from the analysis of tap water are shown in Fig. 3. The baseline was quite stable, and the four THMs and the internal standard (toluene-d8) were separated in less than 1.5 minutes.

Linearity is an important criterion of an analytical system. Calibration curves were established based on the peak area ratio of THMs/toluene-d8. The system was linear in the range of 0.05-90 ppb. Each point on the calibration curves represents the average of three analyses of the standard solutions. The relative standard deviations of the points were in the range from 0.6 to 8.9%, and the correlation coefficients were in the range from 0.996 to 0.999.

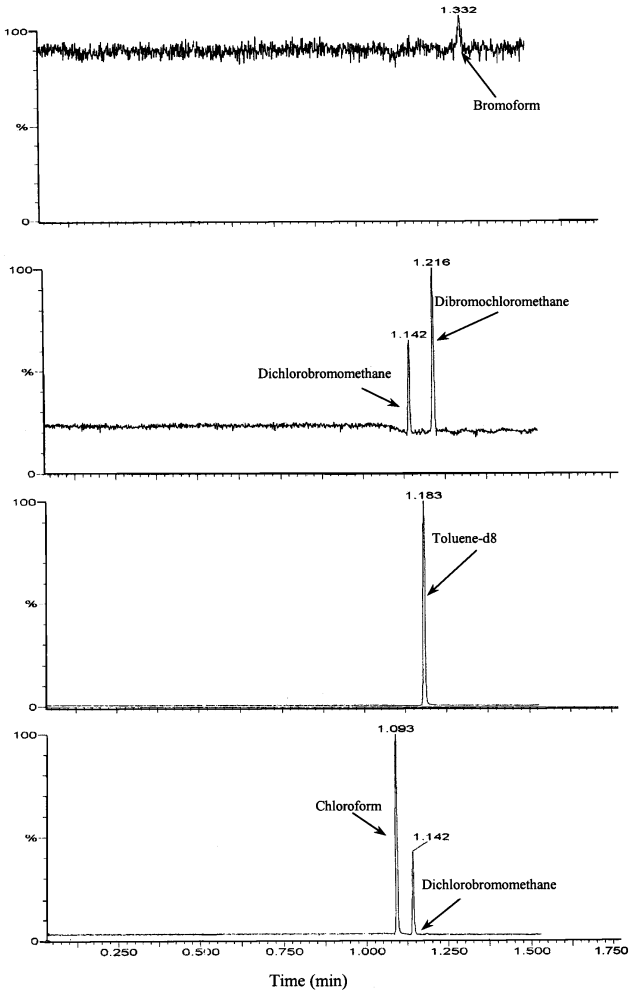

Fig. 3. Mass chromatograms of THMs and internal standard (toluene d-8) obtained from the analysis of Taipei municipal tap water.

The detection limits of this system were evaluated based on signal/noise ratio equals to 3. The detection limits for a 0.5 mL injection were found to be about 50 ppt, 50 ppt, 50 ppt and 20 ppt for chloroform, bromodichloromethane, dibromochloromethane, and bromoform, respectively. These detection limits are poorer than those obtained with continuous introduction fast GC/MS.[11] The relatively poorer detection limits are not unexpected because a steady state is not established in pulse injection membrane extraction GC/MS analysis. Although the detection limits are poorer than the continuous system, [11] they are adequate for the analysis of THMs in tap water because the concentration of THMs in tap water is seldom below 100 ppt.

In practice, automation is needed for continuous on-line monitoring. In this system, the cycle was initiated by the Tekmar 6000 Desorber. The start signal from the Desorber was sent to the GC/MS. In order to synchronize the electrically controlled valve and the analysis cycle, an event signal from the GC/MS was sent to the valve through a homemade relay.

The system has been tested for continuous on-line monitoring of THMs in Taipei municipal tap water. The tap water in the laboratory flowed continuously through the system, and the results of a 10-hour on line monitoring are shown in Fig 4. The concentrations of THMs appeared to be very similar during the 10-hour interval, and the average concentrations of the THMs were 4.6 ppb for chloroform. 3.4 ppb for dichlorobromomethane, 1.4 ppb for dibromochloromethane, and 0.13 ppb for bromoform. To investigate the stability of the system, standard solutions of different concentrations were introduced during the 10-hour monitoring. The results suggested that the system was quite stable during the 10-hour test period (Fig. 4).

CONCLUSIONS

The results presented in this paper demonstrate that, at elevated membrane temperature (70 ℃) and also using inert gas (zero air) as the eluent and as the purging gas, the lag time can be dramatically reduced. Since the carryover from the previous injection was reduced down to less than 5%, the result of each sample pulse represented the true concentration of the sample stream.

This automated pulse sample introduction membrane extraction and fast GC/MS system has demonstrated its capability in on-line and real-time monitoring of THMs in chlori-

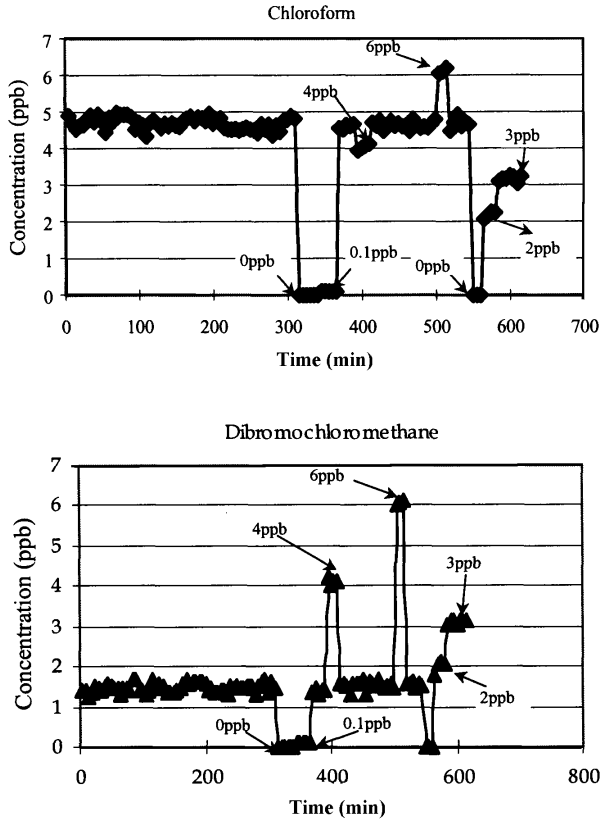

Fig. 4. Concentration vs. time profile of on-line monitoring of chlorinated tap water by pulse introduction membrane extraction fast GC/MS.

nated water. With minor modification, this system is believed to be suitable for on-line and real-time monitoring of other volatile organic compounds in industrial or in environmental samples.

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Key Words

Pulse sample introduction; Trihalomethanes (THMs); On-line monitoring; Chlorinated drinking water; Membrane extraction.

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