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Short communication

On-line monitoring of trihalomethanes in drinking water using continuous-flow purge and cryofocusing gas chromatography–mass spectrometry

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Abstract

A continuous-flow purge-and-trap–GC–MS system was developed for on-line monitoring of THMs (trihalomethanes) in drinking water. Three systems with different traps and purging flow-rates are discussed. In order to minimize interference from water vapor, total purge gas volume and injection temperature were controlled during analysis. Shorter sample concentration time and GC separation time reduced total cycle time to less than 5 min. The detection limits of the system could be lowered to 10 ppt, 25 ppt, 40 ppt, and 50 ppt (w/w) for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$, respectively. This system could detect changes in sample concentration when applied to the on-line monitoring of THMs in drinking water.

Keywords: Purge-and-trap methods; Cryofocusing; Trihalomethanes; Halogenated compounds

1. Introduction

Purge-and-trap–gas chromatography (GC), pioneered by Bellar and Lichtenberg [1,2] in 1974, has been widely used for analyzing volatile organic pollutants in water [3]. Over the years, the introduction of capillary columns and other modifications [4] have improved the method's sensitivity, selectivity, and reliability. The US Environmental Protection Agency (EPA) has also developed several standard methods based on the purge-and-trap technique [5]. Despite their sensitivity and reliability, these methods often require complex and time intensive procedures.

A growing awareness of the importance of trace amounts of volatile organic compounds in drinking water has placed heavy demands on our ability to quickly analyze analytes in concentrations at the ppt level. The purge-and-trap technique has become one of the major methods for analyzing trihalomethanes (THMs) in chlorinated drinking water, and some purge-and-trap methodologies [6,7] have recently been developed to reduce hands-on operator time and increase laboratory output [8]. Systems such as the on-line or an automated system do not require operators to add the internal standard and individually inject each sample, while at the same time avoiding the possibility of contamination and sample loss during analysis. On-line analytical instrumen-

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tation can also in many cases effectively provide the feedback necessary for proper control.

In order to achieve on-line analysis, a continuous-flow purge-and-trap device has been developed. This device was coupled with GC–mass spectrometry (MS) to reduce the analysis time. We applied the system to the on-line monitoring of THMs, disinfection byproducts in drinking water [9].

2. Experimental

2.1. Chemicals and reagents

Trihalomethane compounds of 98% purity were purchased from Aldrich, Avocado, Chem-Service, and Merck. [$^2H_8$]Toluene, purchased from Cambridge Isotope Labs. was used as the internal standard. Stock solutions were prepared by dissolving 100 mg of each compound in 10 ml methanol, respectively. Appropriate amounts of these stock solutions were spiked into 100 ml reagent water to give different concentrations of aqueous stock solutions. The standard solutions were all prepared by diluting aqueous stock solution with reagent water.

2.2. Apparatus

2.2.1. Continuous-flow purge-and-trap sampling device

The continuous-flow purge-and-trap system (Fig. 1) was equipped with a purging vessel consisting of a 20-ml vial with two 7 mm O.D. glass tubes attached, a screw cap with two holes, and a PTFE–silicone based rubber septum. The septum, placed inside the cap, was used to prevent the purging vessel from leaking. The glass vessel was then coupled to the purge-and-trap system by puncturing the septum with two 0.32 mm fused-silica transfer lines. Sample aqueous solutions were introduced into the purge vessel using rotary pump A (Cole-Parmer MasterFlex, Model No. 7518-10) at 50 ml/min, while the internal standard solution was pumped through the T-connector using pump B at 10 ml/min and mixed with the sample aqueous solution in the purge vessel.

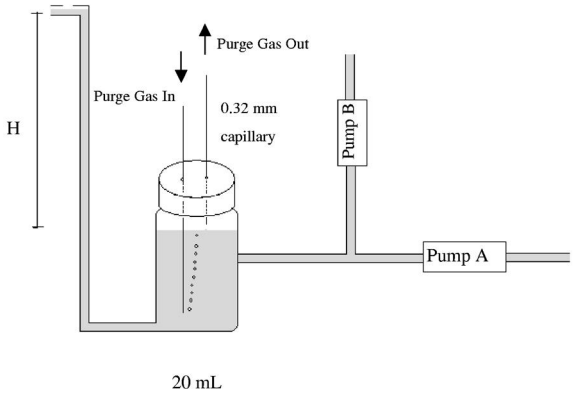

Fig. 1. A continuous flow purging device.

2.2.2. Cryofocusing inlet system and GC–MS

The cryofocusing unit of a Tekmer 6000 AERO Trap Desorber (Rosemount Analytical, Tekmar, Cincinnati, OH, USA) was used to trap and concentrate samples, and then to inject the trapped analytes into the GC–MS system. A Shimadzu QP5050 quadrupole GC–MS system (Shimadzu, Tokyo, Japan) was operated in the selected ion monitoring (SIM) mode to monitor THMs with base peaks of m/z 83, 129, and 173. The interface was set at 250°C, and the ion source temperature was set at 230°C. A 5 m× 0.25 mm I.D. DB-5MS (J&W Scientific, film thickness 0.25 μm) capillary column was used for separation of the THMs. The GC system was operated in the splitless mode.

2.3. Operation systems and procedures

2.3.1. Low-flow purge/adsorbent trap system and low-flow purge/cryofocusing trap system

The continuous low-flow purge/adsorbent trap system (Fig. 2a), was operated first in the sample introduction mode, in which analytes were purged out from aqueous solution by a carrier gas and then trapped at room temperature by a Tenax-TA adsorbent packed in a 0.53 mm I.D. deactivated fused-silica capillary. The length of the packing was 5 cm. After purging for 1 min, the system was changed to the sample injection mode (Fig. 2b) by switching the six-valve switch. The cryofocusing inlet was then heated at a rate of 500°C/min to 200°C, causing analytes trapped on the adsorbent to desorb for injection into the GC–MS system.

The procedures for the low-flow purge/cryofocus-

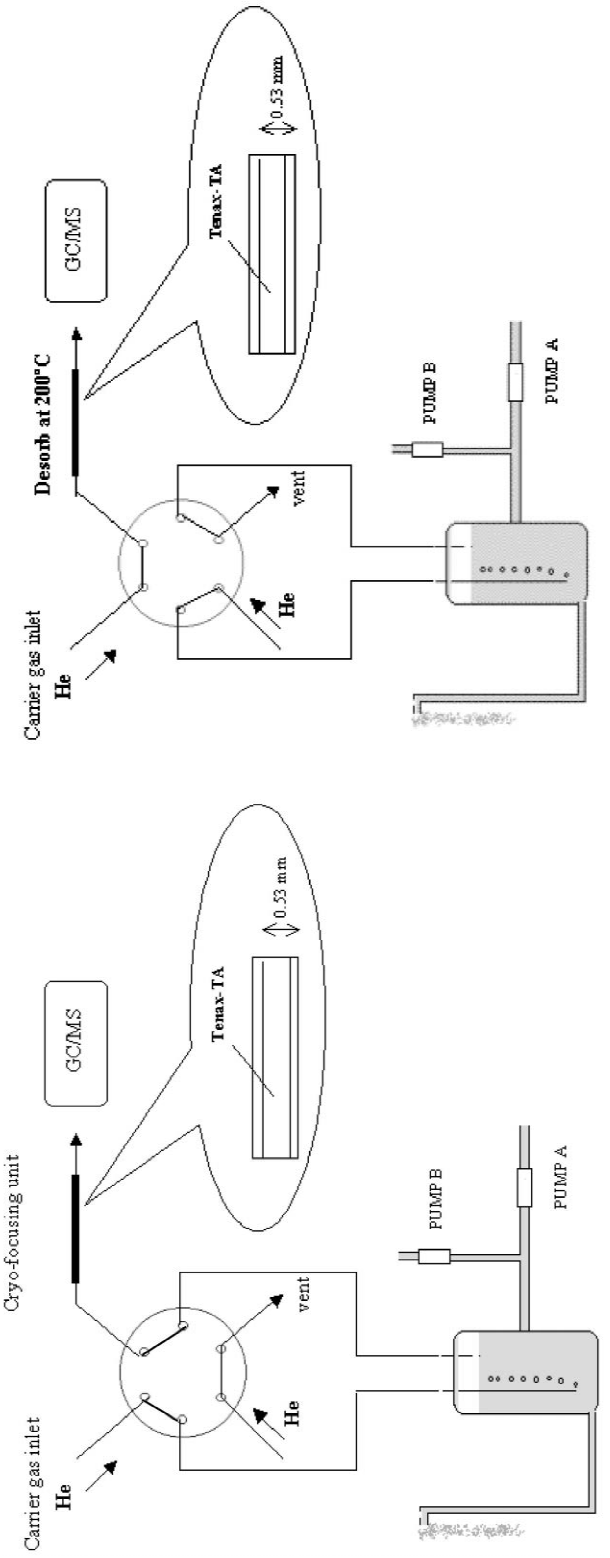

Fig. 2. A low flow purge/adsorbent trap system. (a) Sample introduction mode. (b) Sample injection mode.

ing trap system, were the same as for the continuous low-flow purge/adsorbent trap system, except that the Tenax-TA packed trap column was replaced with a 0.32 mm I.D. fused-silica capillary column, and the cryofocusing unit was cooled to −165°C to trap.

2.3.2. High-flow purge/cryofocusing trap system

In the sample introduction mode (Fig. 3a), the cryofocusing unit was cooled and held at −165°C. THMs were continuously purged out from the sample solution by purge gas B and trapped by the cooled cryofocusing unit. The actual flow-rate of purge gas B could be estimated by a flowmeter connected to the vent. Moreover, helium was introduced into the GC–MS system as the carrier gas, and the flow-rate was kept low so as not to break the vacuum.

After concentrating the THMs in the sample introduction mode, both six-valves switches were switched to the sample injection mode (Fig. 3b), in which the cryofocusing unit was heated from −165°C to 0°C to release the THMs for injection into the GC–MS system by carrier gas A. At the same time, purge gas B was vented into the atmosphere. In order to maintain the continuous purging device, it was necessary to keep the headspace in the purge vessel at a constant pressure consistent with the height of the outflow water. Purge gas C was introduced for this purpose, and also to prevent a sudden drop in pressure that would force the sample solution flowing into the purge gas transfer line.

3. Results and discussion

A design for continuous-flow purge and trap device is shown in Fig. 1, and has been described in the Experimental section. The height of the exit for outflow water, the head pressure of the purging gas, and the inner diameter of the capillary for purging gas determined the headspace pressure of the purging vessel, which in turn determined the flow-rate of the purging gas. The higher the exit for outflow water, the larger the purge gas pressure necessary to maintain the equilibrium of the continuous-flow system. This equilibrium also maintained a constant water level in the purge vessel.

Chemisorption has been reported to overcome the problem of water content in the headspace gas [10]. In the low-flow purge/adsorbent trap system (Fig. 2), we used a hydrophobic polymeric adsorbent (Tenax-TA) to trap purged analytes and prevent the adsorption of purged water vapor. The four THMs were separated in 42 s, but with peak widths in the range of 3 to 4 s. This bandwidth was due to the dead volume caused by thermal desorption of the analytes from the adsorbent. Though further cryofocusing before injection of the analytes could narrow the injection bandwidth, this would lengthen the cycle time.

In the low-flow purge/cryofocusing trap system, we minimized interference from purged water vapor by controlling the sample injection temperature, a strategy previously developed in our laboratory and demonstrated in an earlier work [11]. The cryofocusing unit was cooled and held at −165°C for 30 s so as to concentrate the purged analytes, while trapping any water vapor released during the purging process. The cryofocusing unit was then heated to the sample injection temperature, set at 0°C, and held at this temperature for 40 s, during which the cryfocusing unit condensed and trapped water vapor while injecting the four THMs into the GC–MS system. The resulting peak widths were narrower than for the low-flow purge/adsorbent trap system, and for four THMs were separated in less than 40 s. The detection limits of this system were about 20 ppt, 60 ppt, 100 ppt and 120 ppt (w/w) for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$, respectively.

Since in some cases bromoform concentrations in Taipei's tap water fall near this detection limit, an improvement in the detection limit of this system is necessary. Although a higher purge flow-rate would improve the detection limit by increasing the amount of analytes purged, the flow-rate is limited by the need to maintain the vacuum. In the low-flow purge/cryofocusing trap GC–MS system, the detection limit can be improved with an increase in purging time, however this approach would prolong the cycle time. To overcome this problem, we designed a continuous-high flow purge/cryofocusing trap system (Fig. 3). Unlike the low flow purge and trap system, the vacuum presents no limitation on flow-rate of purging gas. An additional six-valve switch introduced a high-flow-rate purging gas into the purging vessel, which proceeded through the

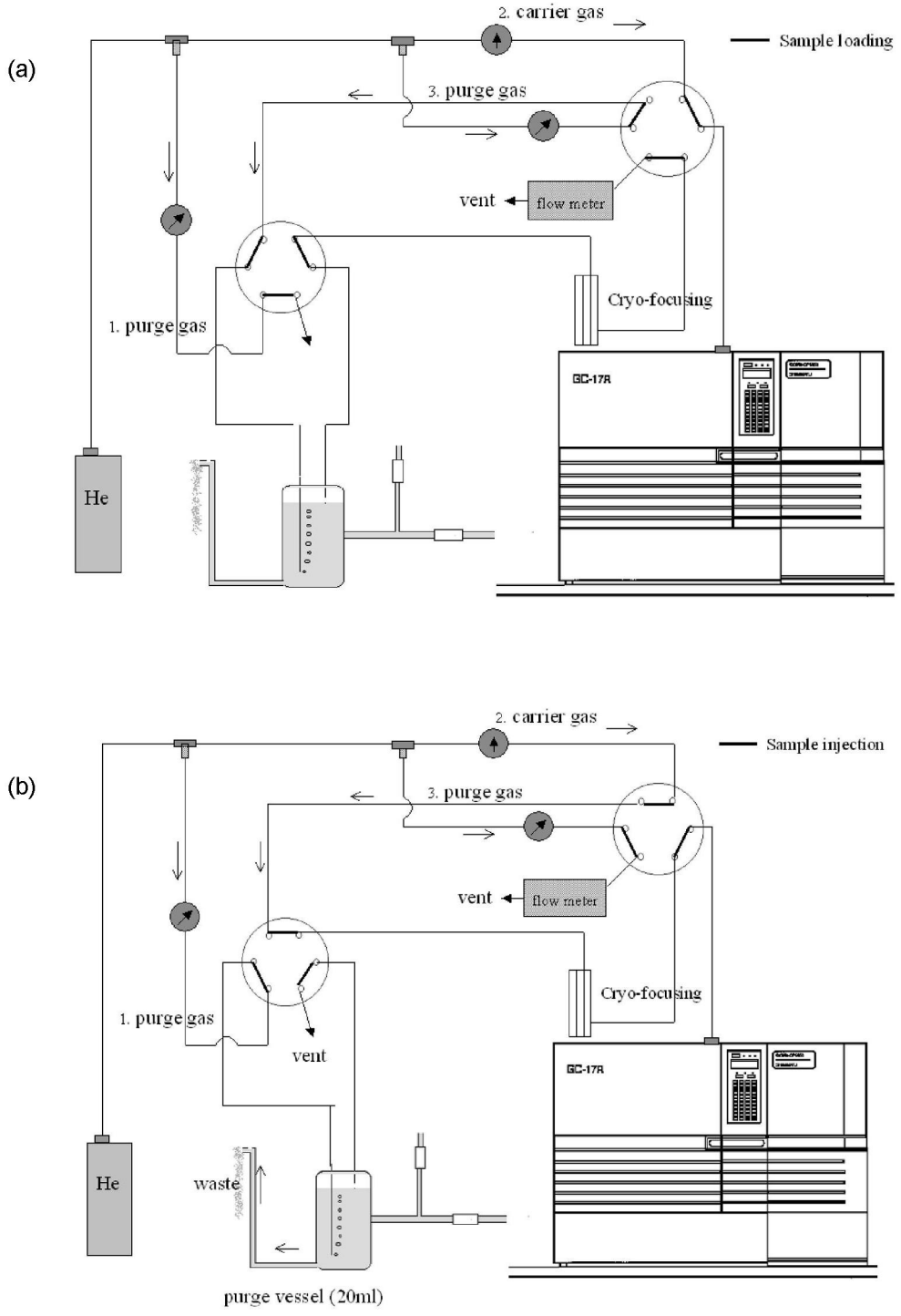

Fig. 3. A high flow purge/cryofocusing trap system. (a) Sample introduction mode. (b) Sample injection mode.

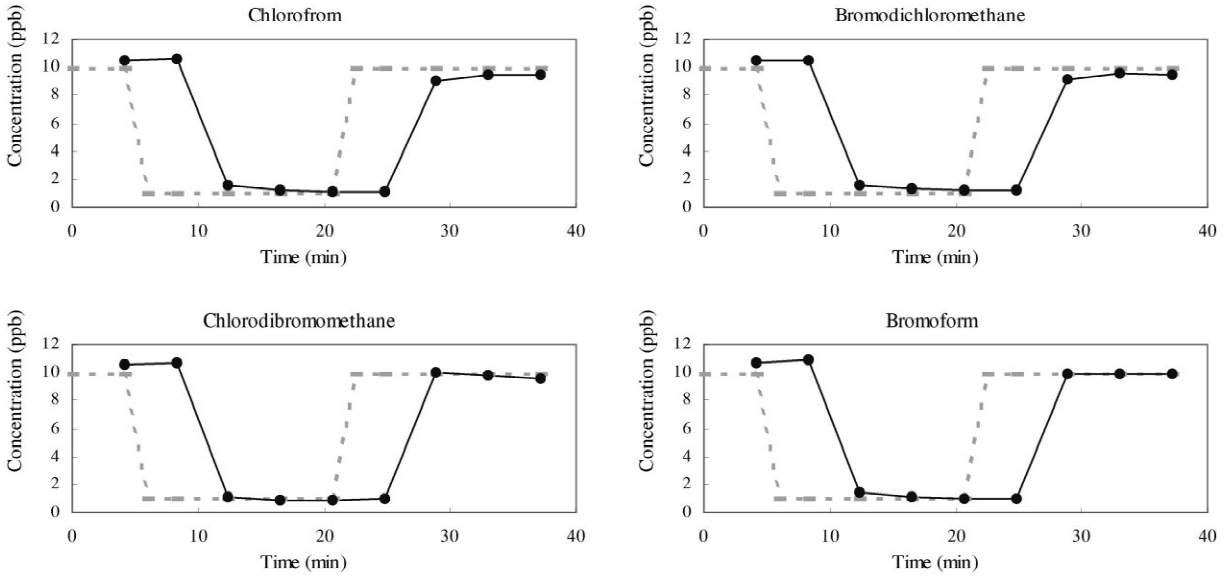

Fig. 4. On-line monitoring a simulating sample concentration change. The dash lines show the sample concentration change, and the solid lines are the concentrations detected by the system.

cryofocusing capillary, finally venting outside the system. The two six-valve switches not only switch between the low-flow carrier gas and the high-flow purging gas, but also maintain a constant headspace pressure in the purging vessel. This permits an increase in the total quantity of analytes purged and trapped during the same amount of time, thus improving detection limits. To avoid frozen ice from clogging the capillary trap, total purge volume was controlled in this approach. With a purge flow-rate of 4.6 ml/min, the compromise between total purge volume and peak resolution resulted in a 0.32 mm capillary trap column and an optimum purging time of 0.5 min.

As the ability to detect changes in sample concentration is important for the on-line monitoring of drinking water, the high-flow purge/cryofocusing trap system was used to analyze such changes. After analyzing for 8.3 min, a 10 ppb sample solution was replaced with a 1 ppb sample solution. 16.5 min later, the 1 ppb solution was replaced with the 10 ppb sample again. Fig. 4 shows the concentrations detected for THMs, and it demonstrates the ability of the system to response the changes in sample concentration. The sample carry-over of THMs ranged from 4.3 to 6.7%. The response lagged behind the concentration change about 5 min. The precision, accuracy, and robustness of the system were tested by on-line monitoring of a 4 ppb standard THM solution. For a 5-h on-line monitoring, the relative standard deviation for each compound ranged from 1.4 to 10.5%. The accuracy, expressed as the percent difference between the known and the measured concentrations ranged from 1.9 to 2.7%. Calibration curves with seven different concentrations from 196 ppt up to 25 ppb were established based on the peak area ratio of THMs/[$^2H_8$]toluene, and the correlation coefficients were in the range 0.994–0.998. The result of a continuous monitoring of THMs in tap water suggested that the concentrations of THMs did not change significantly, and the average concentrations of four THMs in the tap water were 5.4 ppb for $CHCl_3$, 3.38 ppb for $CHCl_2Br$, 1.55 ppb for $CHClBr_2$, and 0.41 ppb for $CHBr_3$.

4. Conclusions

This study demonstrates the on-line analysis capability of the laboratory-made continuous-flow purge-and-trap–GC–MS system. The cycle time can be reduced to less than 5 min, resulting in a maximum frequency of 15 samples/h. Detection

limits of four THMs were at low-ppt levels, and the system is suitable for on-line monitoring of other volatile organic compounds in water as well. Currently, we are working to make the system completely automated.

Acknowledgements

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