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ISOLATION AND DETERMINATION OF VOLATILE ORGANIC COMPOUNDS FROM WATER BY DYNAMIC PURGE-AND-TRAP TECHNIQUE COUPLED WITH CAPILLARY GAS CHROMATOGRAPHY

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The preconcentration technique of purge-and-trap has been investigated in the present work for quantitative adsorption of volatile organic pollutants purged from water samples. A dynamic purging device with variable volume size has been constructed and tested to purge different concentrations of organic compounds. With Tenax GR as the adsorbent, a dynamic purge-and-trap technique was developed combining on-column preconcentration procedures using ambient trapping/thermal desorption/cryogenic focusing/back-flash injection prior to separation and determination using capillary gas chromatography. Various aromatic compounds in water were determined, giving linear working ranges over five orders of magnitude from 0.02 to 5000 µg/L. The analytical procedures were optimized under the assistance of ultrasonication with results validated for the determination of organic contaminants in underground water and tap water, giving over 93% recoveries and a detection limit of 0.01 µg/L, two orders of magnitude lower than those obtained using commercial available instruments with on-line configuration to minimize cross-contamination. The technique provides a potential automated method for *in situ* monitoring of volatile organic compounds in water.

Keywords: Trace determination; Purge-and-trap; Capillary gas chromatography; Volatile organic compounds

INTRODUCTION

The analysis of volatile organic compounds (VOCs) has always been a major challenge for the environmental chemists because they are present at very low concentration in water. More strict regulation for the presence of the VOCs in water down to the µg/L level is now stipulated by the USEPA for drinking water [1,2].

The major problems facing the determination of organic compounds in water are their complicated sample matrices and low concentration. Therefore, it is necessary to preconcentrate the contaminants before analysis. The methods included stripping [3], solvent extraction [4], headspace techniques [5,6], adsorption on solid sorbents [7],

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and full evaporation technique [8,9]. However, the headspace method is lack of sufficient sensitivity and the use of a large volume of sample for injection into the GC column could lead to the reduction of chromatographic resolution. The full evaporation technique can address some of the matrix problems by equilibration at temperatures above the boiling points of the analytes of interest to force them out of the matrix into the headspace [8,9]. However, its sensitivity is more or less the same as the headspace method with insufficient sensitivity for many applications in environmental analysis. Use of organic solvent for solvent extraction leads to additional dilution, reduction in sensitivity, disturbance in chromatographic separation of analytes due to the presence of solvent impurities, and concern about the toxicity of the solvents used. A relatively new technique is the solid-phase micro-extraction (SPME) that is able to address the need for preconcentration of analytes from aqueous solution [10], and the selectivity of analytes can be modified by coating different liquid phases onto the fiber [11]. The sensitivity of SPME had been shown to be about 3 orders of magnitude higher than the headspace method [12]. Although the technique is simple and suitable for analysis of volatile and semi-volatile compounds in water, the SPME methodology requires strict procedures for preconditioning to prevent accidental contamination. Also, the SPME fiber should be kept cool. When the temperature of the fiber increases, the partition coefficient will decrease [13].

The purge-and-trap gas chromatography, at which the VOCs was purged from the water sample by a stream of gases, adsorbed on a trap made of porous solid sorbents and desorbed into GC for separation and quantitation, has become a valuable and widely accepted method for the analysis of VOCs in water. It was adopted by the USEPA in various EPA methods [14]. To increase the detection sensitivity, a simple way is to increase the sample volume. Most of the commercially available purging apparatus are developed for a fixed sample volume. This limits the detection sensitivity and restricts its scope of application for analyzing low concentration of VOCs in environmental samples. Some authors have extended the application of the method by either modifying the purging device [15,16], developing semi-automation [17–19] or using polymer adsorbents, such as Tenax GC, for the preconcentration of organic compounds liberated from aqueous phase [20] prior to separation by packed column or capillary column [21]. It has been applied for the sampling and enrichment of both polar and nonpolar compounds at trace and ultra-trace levels, showing good repeatability [22–24]. However, the detection limits of the various methods are governed by the total amount of VOCs present in the original water sample. Use of dynamic purging does not have such limitation and the detection limit can always be lowered by employing a larger sample volume. Thus, in the present work, an analytical procedure employing a dynamic purging is investigated to optimize its enhancing effect on the detection limit of the purge and trap methodology.

We have successfully used the apparatus developed for various applications in the laboratory since 1991 [25,26]. The use of the device offers many advantages such as convenient to vary the sample volume at different concentrations, operation in a continuous mode, and easy switch to full automation. In the present work, we shall investigate the coupling of the continuous purging device with GC separation and quantitation for the determination of trace levels of volatile organic compounds in environmental samples and hazardous wastes incorporating procedures for on-line trapping, thermal desorption, cryogenic focusing and back-flashing injection to increase the detection sensitivity and minimize cross interference. The maximum achievable

sample volume was discussed. Secondly, the development of a simple purging procedure under the assistance of ultrasonication to increase the removal efficiency was described with an aim to address problems related to automation in chemical analysis for widely different and complicated environmental matrices.

EXPERIMENTAL

Reagents

All reagents were analytical reagent grade (BDH Chemicals or Aldrich) unless otherwise stated. All reagents were used without further treatments. The stock solutions of 1000 $\mu\text{g/L}$ of benzene, toluene, ethyl-benzene, and xylenes standards were prepared by dissolving them in methanol and storing them at 4°C. Standards for calibration were obtained by appropriate dilution from these stock solutions. Mixed standard solutions were prepared from mixing individual stock solutions. The organic standards used for recovery tests were calibrated with external standard solutions.

The organic free water used for the preparation of all aqueous reagents and for recovery test was purified by passing it through ion exchangers with collection at resistivity equal to or higher than 18 mega-ohm per cm as indicated by the conductivity meter of the water purification system. The deionized water obtained was then doubly distilled and purged with several liters of purified helium gas to remove possible volatile organic compounds before use.

All Tenax polymers and adsorbents are purchased from Alltech Associates, Deerfield, IL, USA. Molecular sieve 601 was purchased from Shanghai Reagents Co.

Apparatus

A Raytest 90 digital temperature controller (Germany) was used for thermal desorption of analytes trapped in the purge trap. A Nafion membrane (Perma Pure) drier was placed before the trap so as to reduce the moisture content from the purge gases and avoid column blockage during cryogenic on-column focussing. A Hewlett-Packard gas chromatograph, model 5890 series II, equipped with a flame ionization detector and an electron capture detector was used for quantitative analysis. A Hewlett-Packard 3395 integrator or a data station (self constructed) was employed for data acquisition. The separation of analytes were achieved on a capillary column from Hewlett-Packard (Ultra-1, cross-linked Silicone gum 25 m \times 0.32 mm i.d., 0.52 μm film) or J&W Scientific (DB-624, 30 m \times 0.32 mm i.d., 1.8 μm film thickness coated with cyanopropyl phenyl dimethyl polysiloxane). A Retsch (model USG) ultrasonic generator was used to improve the purge efficiency for volatile organic compounds in water.

Equipment Setup

All experiments were carried out employing a self-constructed on-line dynamic purge-and-trap device. Purgeable organic compounds were trapped and preconcentrated when they were passing through the trap. The purge and trap system is consisted of three separate pieces: a dynamic purging device, a trapper and a desorber. Figure 1

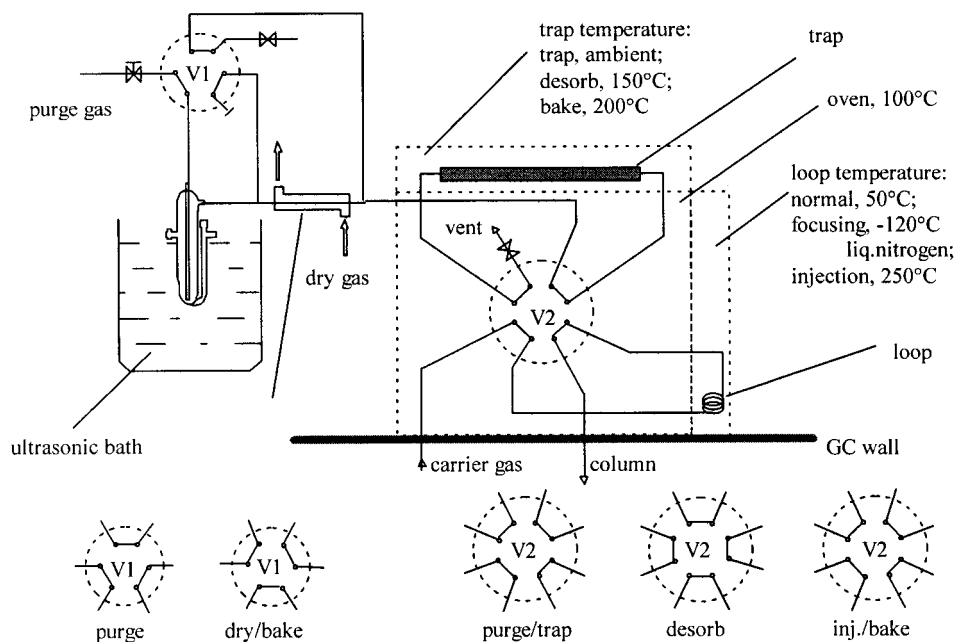


FIGURE 1 A schematic diagram of the adsorption and desorption system.

shows a schematic diagram indicating the operations in sequence for on-line stripping absorption, thermal desorption, cryogenic focusing, back-flash injection, and gas chromatographic separation and quantitation.

The dynamic purging device is shown in Fig. 2. The device has a 15 mL capacity. A stream of helium purge gas was dispersed into finely divided bubbles by a glass frit placed at the bottom of the bubbler to purge the analytes for collection in a trap located at the outlet of the bubbler. Sample can be fed into the scrubber through a Teflon stop valve at the top position of the scrubbing chamber at opposite direction of the gas flow. The volume of samples can be adjusted to any size either manually or by a pneumatic pump feeding. The scrubbing chamber can contain a sample volume of over 100 mL.

Samples to be analyzed were collected in sampling traps. The traps were Pyrex glass tubes with 6.4 mm outside diameter and 200 mm length and packed in the center with 600 mg Tenax GR 60/80 mesh for a length of about 100 mm. Each end of the sorbent bed was kept in position by packing with siliconized quartz wool.

The sampling trap was placed inside a small tube furnace with exchangeable adsorption tubes and under a temperature cycle for trapping (room temperature at about 25°C), desorption (150°C) and baking (200°C). An eight port valve was used to switch the gases at appropriate direction of purging, drying, baking, focusing and injection as shown by the corresponding configurations given in Fig. 1. The valve was placed inside the GC oven to avoid condensation and to ensure a leak-free operation. The system, with exchangeable adsorption tubes, allows a flexibility of either loading adsorption tubes prepurged in the field into the sampling trap or purging laboratory samples to load onto a pre-cleaned trap placed inside the tube

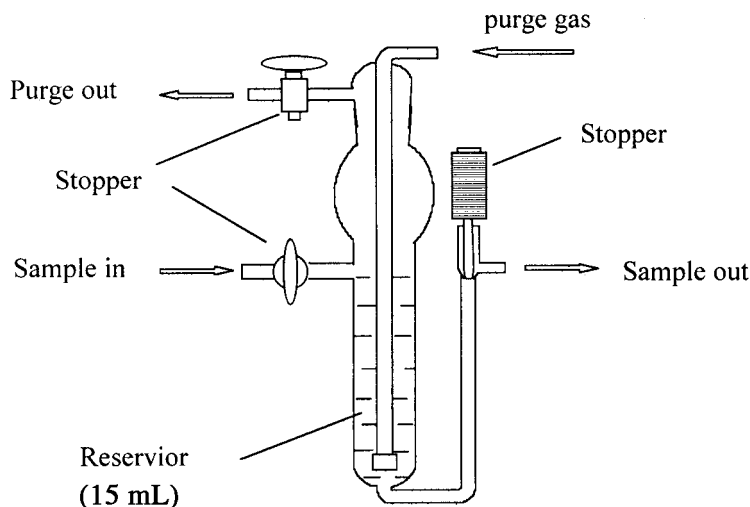


FIGURE 2 A schematic diagram of the dynamic purge device.

furnace through the external lines connected to the purge device. The analytes on the trap can then be desorbed in a back-flash mode by the carrier gas onto the sample loop for cryogenic focusing at a controllable flow rate. Subsequently, the analytes are flash-heated using a second heater for injection onto the capillary column by the carrier gas flow. When the system is first started, it must be pre-purged with the carrier gas to remove oxygen and water so as to reduce the oxidative degradation of the sorbent during the heating cycle. The interface developed provides a satisfactory sample introduction with a narrow band injection and outstanding efficiency.

Operation Procedures

Purging and Absorption

Helium gas (Hong Kong Oxygen Co.) was used as the purging gas after purification through an activated charcoal cartridge and 5 Å molecular sieve trap to remove possible organic compounds and water. Before purging and introduction of sample, the purge-and-trap system was initially set at the purging mode with the sampling trap inlet attached to the purging device and the two valves set at purge position. The purge gas flow rate was adjusted at 50 mL/min. The water samples were equilibrated to ambient temperature prior to being introduced into the bubbler. The removal of volatile organic substances was assisted using ultrasonication. After purging for 10 min, the purging gas was set to bypass the sample container by turning valve V1 clockwise and the trap was dried by maintaining a constant flow rate of the dry purge gas at 50 mL/min for 5 min to remove moisture. The desorption sample tubes were preconditioned before use to eliminate any possibility of cross contamination. Polymeric sorbent of Tenax GR were conditioned in the desorption furnace at the temperature of 300°C for over four hours under a constant flow rate of high

purity nitrogen or helium at 10 mL/min. This assures that the traps are clean and no contamination or cross contamination of sample occurs.

Thermal Desorption

The eight-port valve was turned clockwise to the desorption position. The desorption temperature was increased to 250°C. The sample loop was immersed into liquid nitrogen placed in a thermal flask that could be moved rapidly in and out from the sample loop. The carrier gas was then passed through the trap to sweep the analytes to the cryogenically focused sample loop. The desorption times was 5 min under helium at a constant flow rate of 2 mL/min.

Injection and Trap Backing

When desorption was complete, the valve V2 was turned anticlockwise to the injection position. The heating block maintained at 250°C was inserted into the sample loop to flash-heat the analytes and vaporize them onto the capillary column for separation. Temperature of the desorption device was maintained at 250°C to bake the trap for 10 min under a flow rate of 50 mL/min and it was then cooled to ambient temperature for the next cycle of analysis. After closing both purge outlet and sample outlet of the purge device, the sample after purging can be pushed out from the device to prepared the system for the second sampling.

Sample Preparation

River or seawater was collected below the surface at 0.5–1.0 m. For underground water collection, a hole of 100 mm diameter was drilled at different depths. Water was drawn through a stainless steel sampler and the first several liters were discarded. The cleaned sampling bottle was then washed with the water sample (twice the bottle volume) onsite before filling it up to the top and sealed without leaving any air gap at the bottle cap. The sealed bottle was then transported back to the laboratory for analysis. All the sample bottles used for sample storage were made of glass and heated at 200°C in an oven overnight to remove volatile organic substances. For sample storage up to two weeks, 0.2% nitric acid was added to the sample for preservation. The sample was then stored at 4°C and analyzed within 24 h after collection. Plastic container should not be used because of the possibility of contamination from the container.

Chromatographic Condition

Chromatographic separation of the volatile organic compounds purged out from the water samples was carried out in a capillary column (HP, Ultra-1). The column temperature was programmed as follow: initial temperature at 35°C for 5 min, following by increasing the temperature to 150°C at a constant rate of 5°C/min, and finally holding the temperature at 150°C for 5 min. The detection port temperature were set a 225°C. helium gas was used as the carrier gas at a flow rate of 2 mL/min. The helium make-up gas was set at 30 mL/min.

RESULTS AND DISCUSSION

Optimization of Operation Parameters for Dynamic Purge

The schematic diagram of the dynamic purge apparatus is shown in Fig. 2. From the figure, it can be seen that the purge operation is carried out under countercurrent flow mode of extraction, in which the gas phase is introduced at the bottom of the purge device (desorber) and the liquid sample is introduced at the top. In order to achieve a high sensitivity, the following parameters have to be optimized: sample volume, purging time and breakthrough volume. The sample volume can be flexibly changed from 15 mL to any volume by feeding the water sample from the left top inlet of the system. Practically, the sample size will not be larger than a volume of 1000 mL. For the concentration of volatile organic compounds of interest commonly encountered in the original sample, a sample volume of 100 or 200 mL was sufficient to purge enough analytes for detection in the utilization of this apparatus. There are two ways to introduce the water sample to the purge apparatus, either by pumping the liquid sample with a pneumatic pump or by direct sample feeding as the result of the gravity of the hydrostatic pressure. The flow rate can be easily adjusted by turning the inlet and outlet stoppers to a suitable degree.

The use of countercurrent operation is to enhance system performance, as multiple extractions can occur during the process. The use of the countercurrent process could gradually reduce the analyte concentration in the liquid phase after its entrance into the desorber. This process will lead to an eventual complete removal of the analytes in the solution, given sufficient extraction time. When a gas is passing through the liquid phase, a decrease of the mole fraction of solute in the liquid phase p occurs and at the same time, the mole fraction of the same solute in the gaseous phase will increase, depending on its distribution ratio in the two phases. The mole fraction left behind in the liquid phase will be q as $p + q = 1$. If the gaseous phase is removed and the same volume of fresh gaseous phase appeared for the second extraction, a mole fraction of qp will dissolve into the gaseous phase. The third extraction will give a mole fraction of q^2p and for n th extractions, a mole fraction of $q^{n-1}p$. Therefore, for n -times extractions, the extraction efficiency will be:

$$E(\%) = (1 - q^n) \times 100 \quad (1)$$

It is obvious that the maximum purge efficiency will depend on the extraction time. This is in agreement to the results obtained comparing dynamic purge device to normal purge device in fixed volume. Gas solubilities are frequently given in terms of the Henry's law, which states that the quantity of gas that dissolves in a given quantity of liquid is directly proportional to its partial pressure over the solution:

$$P_A = H_A x_A \quad (2)$$

where P_A is the partial pressure of solute A , x_A is its mole fraction and H_A is its Henry's constant. In most cases, the equilibrium between a gas and a liquid will be expressed in terms of an equilibrium constant or the vapor-liquid equilibrium ratio (K_A) as:

$$y_A = K_A x_A \quad (3)$$

In the gaseous phase, the variation of the mole fraction is shown in the following equation:

$$P_A V_g = nRT \quad (4)$$

where R is the perfect gas constant and V_g is its volume at a given temperature T . Therefore, when the ratio of the gaseous volume to the liquid volume (V_g/V_l) is increased, the extraction efficiency will increase. A long period of purging and a large volume of purging gas will be effective for a complete removal of volatile organic compounds in water sample. However, use of a larger sampling volume may lead to the overloading of the sorbent. Knowledge of the breakthrough volumes for the analytes is necessary in order to ensure complete trapping of the analytes within the trap tube.

The full expression of the breakthrough is defined as the volumes of gas needed to cause the adsorbate to go through a unit weight of the adsorbent bed. This value is often recorded as liters of analyte per gram of sorbent. The relative magnitude of the breakthrough volumes indicate which adsorbent is needed and how long a molecule will reside on the adsorbent before it migrates off [25].

A proper choice of the adsorbent is essential to obtain a successful sampling. Comparing to carboxylic, activated carbon and Tenax GR, the porous polymer, Tenax GR, is the most suitable adsorbent for volatile organic compounds. Activated carbon and carboxylic possess high affinity for water require high desorption temperature. Tenax GR is a poly(2,6-diphenyl-1,4-phenylene oxide) containing about 23% graphitized carbon as an integral part of the material. This is not an admixture. The graphitized carbon is coprecipitated with the Tenax polymer. Tenax GR gives higher breakthrough volumes for most analytes and retains less water than Tenax GC or Tenax TA. This makes it an ideal material for the preparation of adsorbent traps. It is a gray solid polymer, with melting point at 460°C, bulk density from 0.35 to 0.45 g/mL and with no smell. Tenax GR is the best choice for trapping volatile organic compounds such as halogenated and aromatic organic compounds, and it is especially suitable for large volume purging.

The extraction efficiencies also depend on the temperature and ionic strength. The effect due to the ionic strength is important. The purge of volatile organic compounds can be improved by the addition of a salt to the solution due to the salting out effect. Purge and trap efficiency can be improved by raising the purging temperature. The higher the temperature, the better will be the efficiency. However, the use of a higher temperature will lead to the entrance of more moisture into the analytical system. Table I shows that when the purge temperature was increased, the removal efficiency for most aromatic compounds was increased, in particular for the higher boiling point compounds. From the table, it can be seen that, comparing to the purging effects at 25°C and 40°C, the removal efficiencies can be significantly improved from 18.8 to 43.6%. However, the water vapor could be copurged when a higher temperature was used. In order to maintain good working conditions, the purge temperature should not be greater than 40°C.

In order to obtain the optimum volume of purge gas, 15 mL water containing 1.0 µg/L of benzene, toluene, ethylbenzene, and xylenes were purged for 5, 10, and 15 min at a flow rate of 50 mL/min of helium. The results are shown in Fig. 3.

TABLE I The effect of temperature and ultrasonication on the purge efficiency of volatile organic compounds in water samples

	T_1 only 25°C (%)	T_2 only 40°C (%)	$(T_2-T_1)/T_2$ (%)	T_{1U} with ultrasound 25°C (%)	$(T_{1U}-T_1)/T_{1U}$ enhancement to T_1 only (%)	T_{2U} with ultrasound 40°C (%)	$(T_{2U}-T_1)/T_{2U}$ enhancement to T_1 only (%)
Benzene	77.9	95.9	18.8	89.0	12.5	91.0	14.4
Toluene	62.1	80.0	22.4	93.8	33.8	93.1	33.3
Ethylbenzene	28.0	40.1	30.2	48.3	42.0	48.4	42.1
<i>m/p</i> -xylene	18.3	32.4	43.5	40.0	54.3	41.4	55.8
<i>o</i> -xylene	12.4	22.0	43.6	35.9	65.4	37.3	66.6

Flow rate: 50 mL/min of helium. The results given in table are % area as recorded by the integrator.

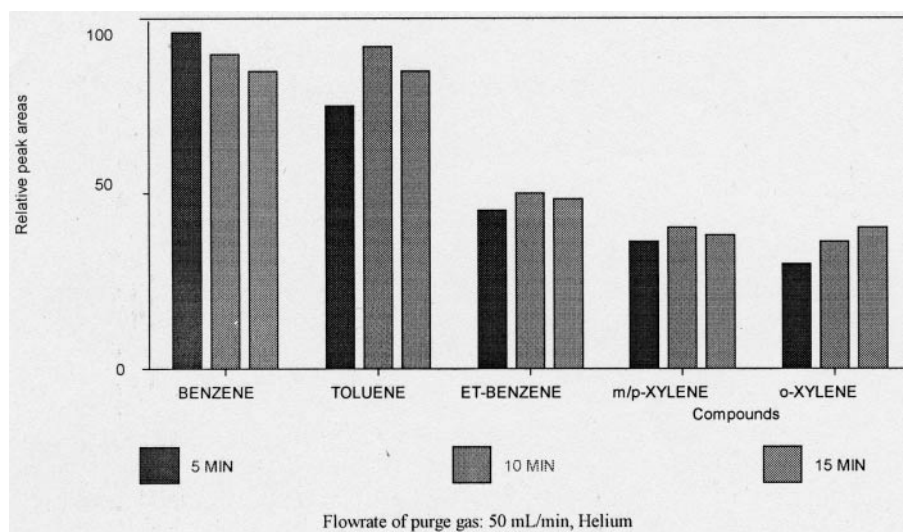


FIGURE 3 Effect of different purge volume.

The optimum volume for benzene is varied from 250 to 500 mL for 5 and 10 min purge respectively, while for toluene and ethylbenzene, their optimum volumes are 500 mL. However, for *o*-oxylene, it is larger than 500 mL. The purging efficiency of a compound is affected by the vapor pressure and activity coefficient of the compounds. The trapping of the compounds is based on the gas-liquid partition. In order to obtain a high sensitivity, the largest possible sample volumes should be used. The purging efficiencies were dependent on the ratio of the purge gas volume, V_g , to the sample volume, V_l [27,28]. The breakthrough volume is different for different compounds. At 500 mL, benzene may have reached its breakthrough volume. A ratio of 10 is reasonable as a 100 mL sample was purged with 1000 mL purge gas in 10 min, $V_g/V_l=10$.

Removal Efficiency Assisted Under Ultrasonic Vibration

When an ultrasonic bath was employed to remove the volatile organic compounds from water, it was observed in Table I that the removal efficiency was significantly increased. The reason for the enhanced removal efficiency may be due to the increase

TABLE II Recovery of volatile aromatic compounds collected from standard mixed solutions at two sets of concentrations from 2 to 5 $\mu\text{g/L}$ and 20 to 50 $\mu\text{g/L}$

VOC	Standard added ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)			Average ($\mu\text{g/L}$)	Average recovery (%)	RSD (%)
		1	2	3			
Benzene	2.20	2.12	1.88	2.29	2.09	95.0	9.8
Toluene	2.11	1.89	2.28	2.09	2.08	98.9	9.3
Ethylbenzene	2.17	2.01	2.25	2.18	2.15	99.1	5.7
<i>m/p</i> -xylene	4.34	4.37	3.98	4.12	4.16	95.8	4.7
<i>o</i> -xylene	4.49	4.43	4.12	4.20	4.25	94.7	3.8
Benzene	22.0	21.5	21.8	22.4	21.9	99.5	2.1
Toluene	42.2	41.6	41.2	40.9	41.2	97.7	2.1
Ethylbenzene	43.4	41.9	42.8	42.5	42.4	97.0	1.1
<i>m/p</i> -xylene	43.4	42.3	41.5	41.9	41.9	96.5	1.0
<i>o</i> -xylene	44.9	42.0	43.8	42.6	42.8	95.4	2.1

in temperature and the creation of pressure pulses in the liquid during ultrasonication that are in favor of the distribution of analytes in the gaseous phase. A comparison of the temperature and the ultrasonic effect was also listed in Table I. In the table, the efficiencies have been increased from 12.5 to 65.4%, which are higher than those due to the temperature effect alone on purging. Nevertheless, if ultrasonication was used during purging, the difference between 25 and 40°C is insignificant.

Recovery tests for volatile organic compounds in water have been investigated using two sets of samples at two different concentrations. The first set consisted of volatile aromatic compounds at concentration lower than 5 $\mu\text{g/L}$ and the second was volatile aromatic compounds at higher concentrations. The results obtained are given in Table II. From the table, it is obvious that the average recoveries are satisfactory ranging from 94.7 to 99.1%. For the lower concentration of the volatile organic compounds in water, the relative standard deviation is between 4.7 to 9.8%. The results for the higher concentration volatile aromatic compounds in distilled water show that the desorption efficiency for such a concentration is also satisfactory. The recoveries were ranged from 95.4 to 99.5% and the calibrated standard deviations ranged from 1.0 to 2.1% of the aromatic compounds in water. These results show that the method is well suitable for the determination of benzene, toluene, ethylbenzene, *o*- and *m/p*-xylene in water.

Applicability of the Method for Analyzing Volatile Organic Substances in Water

The calibration curves for the five volatile aromatic compounds studied in this work are listed in Table III. All quantification was based on peak area measurements. A linear dependence of the peak area on the amount injected is evident for volatile aromatics such as benzene, toluene, ethylbenzene, *m/p*-xylene and *o*-xylene, from their detection limit up to 1.0, 2.0, 3.0, 5.0 and 5.0 mg/L , respectively in water.

Under the optimum conditions, the detection limits for volatile aromatic compounds in water are also listed in the table. The detection limits for benzene and toluene are 0.01 and 0.02 $\mu\text{g/L}$, while for other volatile aromatic compounds, they are ranging from 0.03 to 0.05 $\mu\text{g/L}$ in a 100 mL sample solution.

Several samples were collected from a residential construction site at different depths below the ground level at an interval of every 0.5 m. The site was previously used as a

TABLE III Analytical parameters for the determination of various volatile aromatic compounds in water

	Linear working range		A	B	r
	Lower ($\mu\text{g/L}$)	Upper ($\mu\text{g/L}$)			
Benzene	0.01	1.0	1.2047	0.9912	0.9950
Toluene	0.02	2.0	1.0891	1.0043	0.9918
Ethylbenzene	0.03	3.0	0.8590	0.9983	0.9982
Mxylene	0.05	5.0	0.7103	1.0221	0.9938
Oxylene	0.05	5.0	0.5405	1.0393	0.9929

* $y = A + Bx$; $y = \log(\text{peak area})$; $x = \log[\text{VOC}]$; $r = \text{correlation coefficient for the linear test with } n = 6 \text{ for all VOC tested.}$

TABLE IV The analysis of volatile aromatic compounds purged from underground water collected in the field

	Benzene		Toluene		Ethylbenzene		m/p-xylene		o-xylene	
	Mean ($\mu\text{g/L}$)	Recovery (%)	Mean ($\mu\text{g/L}$)	Recovery (%)	Mean ($\mu\text{g/L}$)	Recovery (%)	Mean ($\mu\text{g/L}$)	Recovery (%)	Mean ($\mu\text{g/L}$)	Recovery (%)
TP1	62	95.6 \pm 4.8	14	95.6 \pm 11.0	42	99.9 \pm 10.5	77	98.0 \pm 11.3	38	100.5 \pm 10.3
TP2	60	96.9 \pm 5.7	20	98.3 \pm 4.4	11	93.4 \pm 9.5	16	94.6 \pm 9.1	18	98.3 \pm 11.0
TP3	147	97.3 \pm 0.7	131	99.6 \pm 1.0	51	102.1 \pm 4.1	114	99.0 \pm 2.8	71	96.8 \pm 7.0
TP4	65	98.5 \pm 1.9	62	97.4 \pm 0.9	34	96.8 \pm 2.7	125	96.7 \pm 3.1	52	102.3 \pm 11.0
TP5	68	97.8 \pm 2.4	22	96.7 \pm 2.9	154	98.4 \pm 5.5	330	95.3 \pm 6.8	285	93.5 \pm 4.7
TP6	74	96.9 \pm 4.7	28	97.0 \pm 5.7	168	97.8 \pm 1.7	353	98.4 \pm 5.7	319	95.8 \pm 1.2
TP7	130	98.1 \pm 4.7	17	99.3 \pm 2.4	307	96.7 \pm 2.3	241	94.8 \pm 4.3	324	96.7 \pm 3.2
TP8	56	99.5 \pm 3.1	2	94.5 \pm 13.2	8	95.3 \pm 8.7	43	97.6 \pm 4.8	20	96.1 \pm 14.8

50 $\mu\text{g/L}$ of each standard was added to the underground water for testing the recovery, $n = 4$.

gas station for automobiles with oil tanks built underground. Various sampling points in the site were monitored throughout the construction period. The presence of aromatic compounds in the water collected can be used as an indicator for underground water contamination caused by the leakage of the oil tanks.

Selected volatile organic compounds were analyzed and the results were listed in Table IV. The overall recovery of greater than 93% was obtained for all aromatic compounds in the groundwater sample. It indicated that this technique is useful for the analysis of trace volatile organic compounds in water.

CONCLUSIONS

To enhance the sensitivity for the determination of volatile organic pollutants purged from water samples, a dynamic purging device with variable volume size has been constructed and tested in the present work for its purging efficiency for different concentrations of volatile organic compounds. With Tenax GR as the adsorbent and under the assistance of ultrasonication, a dynamic purge-and-trap technique was developed combining on-column preconcentration procedures using ambient trapping/thermal desorption/cryogenic focusing/back-flash injection prior to separation and determination using capillary gas chromatography. Various aromatic compounds such as benzene, toluene, ethyl-benzene, *o*- and *m/p*-xylene were determined, giving linear working ranges over five orders of magnitude from 0.02 to 5000 $\mu\text{g/L}$.

Under the optimum conditions, the detection limits for benzene and toluene are 0.01 and 0.02 µg/L, while for other volatile aromatic compounds, they are ranging from 0.03 to 0.05 µg/L in a 100 mL sample solution. The detection limits obtained are two orders of magnitude lower than those obtained using commercial available instruments with on-line configuration to minimize cross-contamination. To validate the reliability of the method developed, recovery test was performed on a large number of field underground samples by spiking, and all samples show over 93% recoveries.

The results show that the method is well suitable for the determination of trace levels of benzene, toluene, ethyl-benzene, *o*- and *m/p*-xylene in water and provides a potential method for *in situ* automated monitoring of volatile organic compounds in water.

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