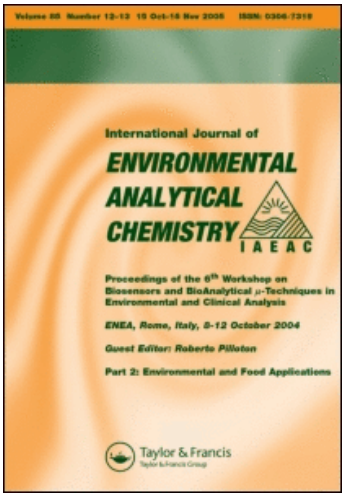

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CONTINUOUS PERMEATION SAMPLER FOR MONOCYCLIC AROMATIC PRIORITY POLLUTANTS IN WATER

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A method for continuous monitoring or off-site analysis of monocyclic aromatic priority pollutants in water is described. The monocyclic aromatics permeate through a polymeric membrane and are purged by an inert gas stream into a sampling tube packed with Tenax-TA. The samples are then thermally desorbed into a capillary column gas chromatograph. This sampler has advantages over conventional methods, such as eliminating time-consuming preconcentration procedures and avoiding the need for an organic solvent. Seven monocyclic aromatics with concentration of from low to mid-μg/L can be detected using one hour sampling time.

Keywords: Membrane permeation; continuous sampler; thermal desorption

INTRODUCTION

Monocyclic aromatics are a group of compounds within the list of 129 priority pollutants[1]. Many analytical methods have been developed to analyze monocyclic aromatics in water, including GC, GC-MS, and HPLC. Considering their low concentration levels in ambient waters, preconcentration is a necessary step before detection. Solvent extraction is a widely used classical method. The currently recommended approach (EPA method 625)[2] is to take two liters of an aqueous sample and adjust the pH to above 11. An initial extraction with 250 mL of methylene chloride is conducted followed by two additional extractions with 100 mL methylene chloride. The extracts are combined, dried, and concentrated to 1.0 mL using a Kuderma-Danish concentrator. The method suffers obvious drawbacks, such as long pretreatment time, the large amount of solvent required, and poor accuracy and precision from losses during sample handling.

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Adsorption/solvent extraction[3,4] and adsorption/thermal desorption[5,6] based on adsorbent columns or cartridges have been applied to the concentration and determination of trace aqueous semivolatile organic compounds. Other new methods, such as spray extraction[7], dynamic stripping/thermal desorption[8], solid-phase microextraction[9], and simultaneous separation and determination by a two-step microcolumn [10] have also been studied to detect trace amount of organic pollutants in water, including some monocyclic aromatics. However, most of the methods rely on complicated procedures and are difficult to perform on a routine basis.

Membrane permeation provides an alternative sampling technique and has been used to passively collect priority pollutants in air[11] and water[12,13]. The application of this sampling method as a field sampler for monocyclic aromatics has been studied recently[14]. Organic pollutants are allowed to permeate through the membrane and then collected by an adsorbent. Either solvent extraction or thermal desorption is then employed to recover the compounds. Tenax-TA is the desired adsorbent for thermal desorption due to its outstanding thermal stability (up to 350°C)[15]. However, the field sampler only provides time-weighted-average concentrations and may not be suitable for monitoring of sample streams subject to rapid changes in concentration. An approach that combines permeation sampling and thermal desorption was first proposed for the determination of phenols in water[16]. The applicability of this type of permeation sampler for monocyclic aromatics is of interest because it allows for the analysis of a single grab or composite type of water sample, or alternatively, continuous monitoring of an effluent stream. In this paper, the monocyclic aromatics permeating through a silicone polycarbonate membrane in a permeation cell are purged into a sampling tube containing Tenax-TA. Thermal desorption is applied to recover the compounds after which sampling and quantification is achieved by capillary gas chromatography. This simple and solvent-free approach should provide for rapid quantification of monocyclic aromatics in water.

EXPERIMENTAL

Reagents

Reagent grade monocyclic aromatic priority pollutants including 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, nitrobenzene, 2,4-dinitrotoluene, and 2,6-dinitrotoluene were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI). Stock solutions containing a single compound with concentrations from 25 mg/L to 100 mg/L were prepared in distilled water and chilled until use. The testing solutions were prepared by appropriate dilution.

Tenax-TA (60/80 mesh, Alltech Associates, Inc., Deerfield, IL) was washed with acetone followed by thermal treatment in a furnace at 300°C for 12 hours in a stream of nitrogen gas of 6 mUmin.

Apparatus

The construction of the permeation cell [17] and the complete continuous permeation sampler system[16] have been described previously. The general experimental set up is shown in Figure 1. The cell consisted of two halves made of stainless-steel with an inner diameter of 7.2 cm, i.e., an exposure area of 40.7 cm^2, and a volume of 10.2 cm^3. This allowed aqueous solution and gas flow through the cell. A 0.038 mm thick silicone polycarbonate membrane (Mempro Membrane Products Company, Troy, NY) was situated between the two halves. A nickel screen was placed on the gas side of the membrane to provide support for the membrane.

A thermal tube desorber, Model 850 (Environchem Inc., Kemblesville, PA) was connected to a Hewlett Packard 5890 gas chromatograph equipped with a HP-5 fused silica capillary column (15 m × 0.25 mm × 0.25 μm film thickness, Hewlett Packard) and a flame ionization detector. Thermal desorption tubes with a dimension of 6 mm o.d. × 4 mm i.d. × 115 mm length were thermally conditioned at 300°C for three hours with a nitrogen gas purge at 30 mL/min prior to use. Silanized glass wool, which was used to seal both ends of the thermal desorption tubes, was treated in the same way to reduce contamination.

Sampling and analysis

The continuous permeation sampler was designed to be used in a laboratory rather than field sampling. For this reason, the pH and temperature of the exposure solution could be optimized to obtain higher sensitivity for the compounds under study. An aqueous solution, which contained monocyclic aromatic priority pollutants, flowed from the solution reservoir through the solution side of the permeation cell at a flowrate of 8 mL/min. The solution was in continuous contact with one side of the membrane. Helium was allowed to flow across the surface of the other side of the membrane at 15 mL/min, thus the monocyclic aromatics permeating through the membrane were purged into a sampling tube packed with 0.15g Tenax-TA adsorbent. The permeation cell was maintained at 35°C in a water bath. The flow lines for both water solution and carrier gas were elongated and immersed in a water bath so that the temperatures of the water solution and the carrier gas were close to that of the permeation membrane when they flowed through the permeation cell.

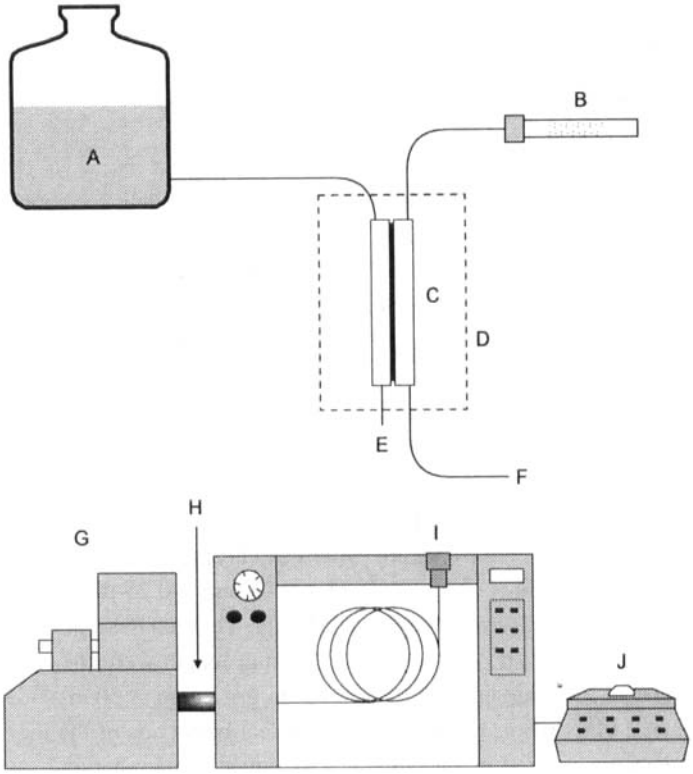

FIGURE 1 Overall Membrane Extraction Design. A) Solution Reservoir; B) Thermal Desorption Tube; C) Permeation Cell; D) Constant Temperature Bath; E) Waste; F) Helium In; G) Thermal Desorption Unit; H) Heated Transfer Line; I) FID; J) Integrator

To ensure that all of the monocyclic aromatics had reached steady state, sampling was not started until the solution passed through the permeation cell for one hour. The amount of the sample collected on the adsorbent was directly proportional to the exposure concentration and sampling time[17]. An one hour sampling time was used to evaluate the performance of this sampler. All exposure solutions were maintained at pH 7.0 since earlier results[14] indicated a slight pH effect for 2,4-dinitrotoluene and 2,6-dinitrotoluene when pH was below 4.5 or above 9.0.

After sampling, the thermal desorption tube was inserted into the thermal desorption chamber and then desorbed at 300°C for 4 minutes. Throughout the study, the temperature of the valve compartment of the thermal desorption unit was set at 245°C while a transfer line temperature of 250°C was used.

RESULTS AND DISCUSSION

Thermal desorption recovery study

To evaluate the thermal desorption recovery of the monocyclic aromatics on Tenax-TA, a 1.00 μL aliquot of a standard solution containing 200 ng/μL per compound was injected into a thermal desorption tube packed with Tenax-TA adsorbent. Thermal desorption was conducted at temperatures ranging from 225°C to 300°C for 5 minutes. The thermal desorption recovery was determined by comparing with the results obtained in an empty thermal desorption tube under the same condition. The method proposed by Pankow et al.[6] was to evaluate thermal desorption recovery. For triplicate thermal desorption runs on Tenax-TA, the quantity D_i = (peak area i)/(peak area naphthalene) was determined. The analogous quantity I, was determined for triplicate on-tube injection runs without Tenax-TA. If it's assumed that all losses of sample species after thermal desorption, e.g., those in transfer line and column,were either negligible or occurred in a linear manner, the $D_i/I_i = 1.0$ would indicate a thermal desorption efficiency of 100% for compound i on Tenax-TA.

The results of the thermal desorption recovery study for all seven monocyclic aromatics at different temperatures are given in Table I. It can be seen that over 90% recovery can be obtained when thermal desorption temperature is 300°C. Recovery data collected at 300°C for different period of desorption time suggested that 4 minutes was appropriate to obtain high recovery as shown in Table II. It was also observed that the FID response for 2,4-dinitrotoluene and 2,6-dinitrotoluene as significantly lower than for the other monocyclic aromatics.

TABLE I Thermal Desorption Recovery of Monocyclic Aromatics

Compound	*Recovery (%)*			
	225°C	*250°C*	*275°C*	*300°C*
1,2-dichlorobenzene	100	103	99	102
1,3-dichlorobenzene	91	98	101	104
1,4-dichlorobenzene	90	97	103	94
1,2,4-trichlorobenzene	94	83	94	98
nitrobenzene	86	90	92	93
2,4-dinitrotoluene	13	69	75	95
2,6-dinitrotoluene	37	69	86	102

TABLE II Thermal Desorption Recovery at 300°C Versus Desorption Time

Compound	Recovery (%)				
	1 min.	*2min.*	*3 min.*	*4 min.*	*5 min.*
1,2-dichlorobenzene	91	102	101	102	100
1,3-dichlorobenzene	94	103	102	104	100
1,4-dichlorobenzene	95	101	99	94	100
1,2,4-trichlorobenzene	71	101	102	98	100
nitrobenzene	0	52	80	93	102
2,4-dinitrotoluene	0	25	78	95	96
2,6-dinitrotoluene	0	32	73	102	96

Evaluation of sampling temperature

Elevated exposure temperature can increase the permeation rates for both analytes and water. In order to enhance permeation rate while maintaining reasonable low level of water permeating through the membrane, the sampling temperature was evaluated. The compound permeating through the membrane was directed into a flame ionization detector by helium and the permeation signal was recorded by a strip chart recorder. By changing the temperature setting of the water bath, the impact of the sampling temperature on response and signal to noise ratio was evaluated. S/N was calculated by measuring the response and its maximum fluctuation in the steady state.

Increasing sampling temperature enhanced the permeation rate exponentially, which is demonstrated in Figure 2. In addition, the time required to reach steady state permeation decreased with the temperature as indicated in Figure 3. However, the amount of water permeating through the membrane increased with the temperature resulting in intense fluctuation of the signal. From Figure 2, it can be seen that when the temperature was above 25°C, the permeation rate increased dramatically with respect to the temperature, whereas the signal to noise ratio showed a steady decline. When the temperature was above 36°C, the signal to noise ratio drastically decrease and the FID was often quenched by excessive water vapor. As a consequence, 35°C was chosen as the sampling temperature.

Calibration of continuous sampler

The following general equation is used to describe the permeation sampler:

$$m = KCt$$

Where K is the permeation constant in ng $\mu g^{-1}L\ h^{-1}$, C is the concentration of exposed solution in μg/L, t is exposure time in hours, and m is mass collected in ng. The permeation constant is dependent on film thickness, exposure area, temperature, and the nature of each compound. For a particular permeation cell, fixed sampling temperature and sampling time, the mass collected on the adsorbent is proportional to the concentration of the compound in the solution.

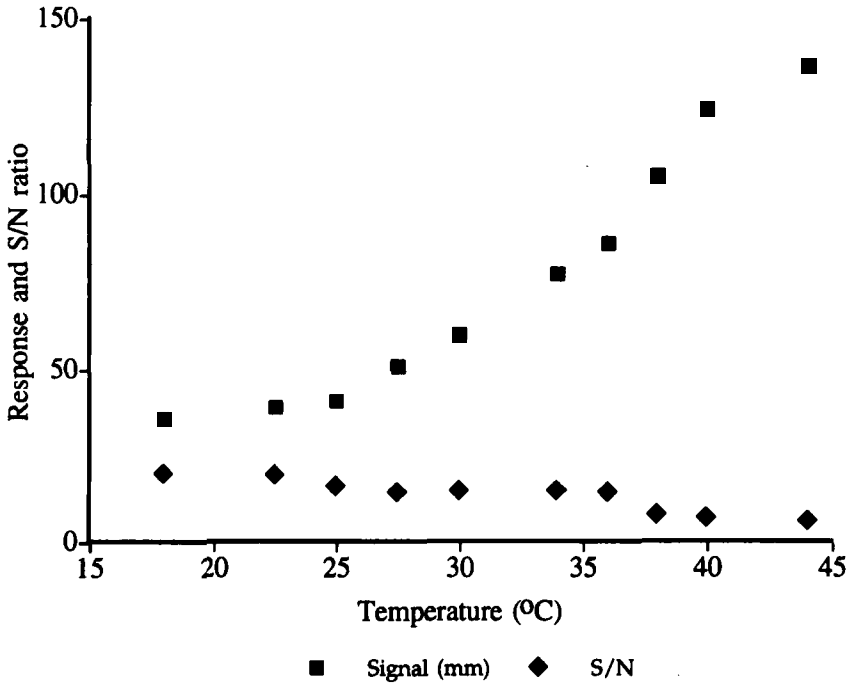

FIGURE 2 Effect of Sampling Temperature on Response and Signal to Noise Ratio

To calibrate the continuous sampler, the permeation cell was exposed to solutions with monocyclic aromatic pollutant concentrations ranging from low to mid- μg/L level for one hour at 35°C. A plot of mass collected on the Tenax-TA adsorbent versus concentration for 1,4-dichlorobenzene indicated a linear relationship (Figure 4). Table III contains permeation constants, concentration ranges and correlation coefficients for seven monocyclic aromatic priority pollutants. All compounds demonstrated a high degree of linearity over these ranges. However, when the concentration was above 350 μg/L, the capillary column became overloaded, degrading the separation. A shorter sampling time should be used when higher concentration samples are to be analyzed.

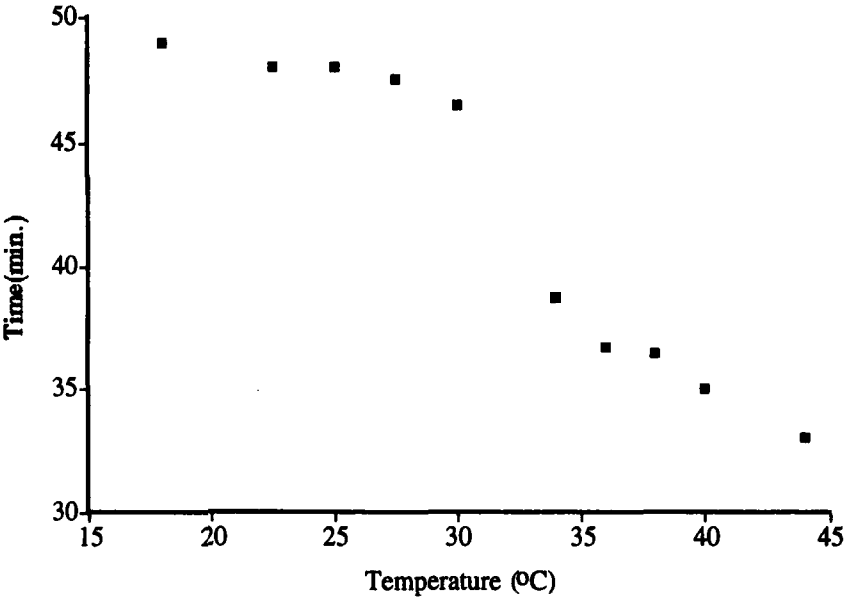

FIGURE 3 Effect of the Sampling Temperature on Time Required to Reach Steady State Response

TABLE III Calibration Results for Continuous Sampler*

Compound	*Concentration. Range* ($\mu g\ L^{-1}$)	*Permeation Constant* ($ng\ \mu g^{-1}\ L\ h^{-1}$)†	*Correlation Coefficient*	*Detection Limit* ($\mu g\ L^{-1}$)+
1,2-dichlorobenzene	7.84–300	21.2 ± 1 28	0.984	2.6
1,3-dichlorobenzene	7.72 – 300	21.6 ± 1 40	0.991	2.3
1,4-dichlorobenzene	5.00–300	17.8 ± 0.893	0.993	3.2
1,2,4-trichlorobenzene	8.72–450	15.5 ± 1.15	0.993	3.6
nitrobenzene	7.18–550	6.19 ± 0.447	0.992	6.5
2,4-dinitrotoluene	750 – 10000	0.356 ± 0.0175	0.989	370
2,6-dinitrotoluene	500–5000	0.596 ± 0.0277	0.987	280

*: Sampling temperature: 35°C; sampling time: 1 hour; pH: 7.
†: Confidence interval: 95%, t-test.
+: Confidence interval: 99%, t-test

Detection limits

To determine the detection limits for the continuous sampler, the permeation cell was exposed to a solution of monocyclic aromatics at the concentrations approx-

imately three to five times the estimated detection limits for one hour at 35°C. Seven samples were collected, thermally desorbed, and analyzed by gas chromatography. The detection limits for the seven monocyclic aromatics are listed in Table III. The results are reported with a 99% confidence interval. A number of modifications can be applied to further lower the detection limits, including prolonging sampling time, increasing the surface area of the membrane, and raising exposure temperature, although potential problems can be caused by higher temperature as discussed previously.

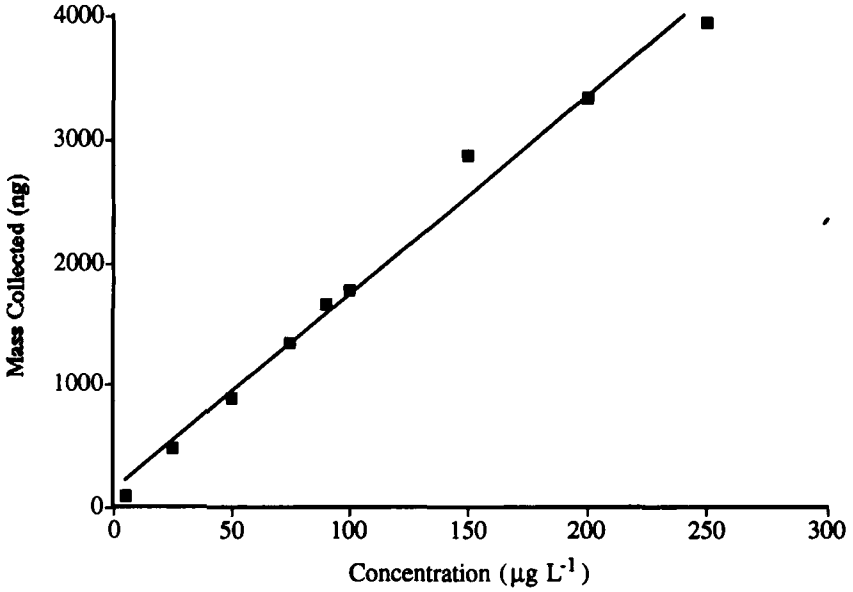

FIGURE 4 Calibration Curve of Continuous Sampler for 1,4-dichlorobenzene

TABLE IV Precision and Accuracy of Continuous Sampler

Compound	*Concentration (μg L^{-1})*	*RSD (%)*	*Accuracy (%)*
1,2-dichlorobenzene	26.2	5.3	96
1,3-dichlorobenzene	25.7	2.0	93
1,4-dichlorobenzene	25.0	1.8	104
1,2,4-trichlorobenzene	30.7	3.2	92
nitrobenzene	47.8	7.8	96
2,4-dinitrotoluene	2500	4.7	91
2,6-dinitrotoluene	2500	5.9	110

Precision and accuracy

To evaluate applicability of this sampler, the permeation cell was exposed to a distilled water solution spiked with monocyclic aromatics at concentrations approximately ten times that of the detection limits for one hour at 35°C. The precision is calculated on the basis of standard deviation of the results obtained from four samples and accuracy is the ratio of the concentrations calculated from the calibration curves and the concentrations spiked. Precision and accuracy results are given in Table IV.

Analysis of spiked authentic water samples

To assess the performance of the continuous sampler in different matrices, wastewater samples were obtained from a local wastewater treatment plant that employs the activated sludge process to treat industrial and sewage wastewater. The water samples represented untreated raw influent and treated final effluent. The samples were spiked with seven monocyclic aromatic compounds. For each matrix, four samples were collected, thermally desorbed, and quantified by GC. The results as well as several water quality parameters are shown in Table V, and indicate that the water matrix has little impact on the continuous permeation sampling method.

TABLE V Results of Spiked Authentic Wastewater Analysis Using Continuous Sampler*

Compound	*Spiked Level* ($\mu g\ L^{-1}$)	*Raw Influent Recovered*		*Final Effluent Recovered*	
		($\mu g\ L^{-1}$)	*Percent*	($\mu g\ L^{-1}$)	*Percent*
1,2-dichlorobenzene	26.1	23.7 ± 1.34	90.8 ± 5.13	26.6 ± 2.60	102 ± 9.96
1,3-dichlorobenzene	25.8	24.6 ± 1.90	95.3 ± 7.36	25.8 ± 0.648	100 ± 2.51
1,4-dichlorobenzene	30.0	29.7 ± 2.27	99.0 ± 7.57	28.7 ± 0.722	95.7 ± 2.41
1,2,4-trichlorobenzene	36.4	39.5 ± 6.15	109 ± 16.9	35.2 ± 3.16	96.7 ± 8.68
nitrobenzene	47.8	46.0 ± 7.78	96.2 ± 16.3	47.1 ± 3.94	98.5 ± 8.24
2,4-dinitrotoluene	2500	2700 ± 467	108 ± 18.7	2340 ± 280	93.6 ± 11.2
2,6-dinitrotoluene	2500	2263 ± 403	90.5 ± 16.1	2309 ± 303	92.4 ± 12. 1
Additional Parameters					
pH		6.5		6.9	
BOD-5 day ($mg\ L^{-1}$)		192		4	
COD ($mg\ L^{-1}$)		413		38	
TSS ($mg\ L^{-1}$)		328		3	

*: Average of four replicate samplings, 95% confidence level, sampling time of one hour at 35°C.

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