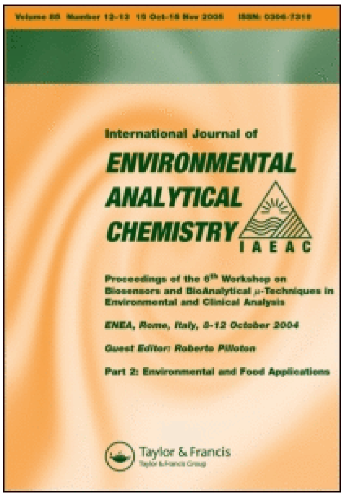

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# Passive Sampling of Monocyclic Aromatic Priority Pollutants in Water

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# PASSIVE SAMPLING OF MONOCYCLIC AROMATIC PRIORITY POLLUTANTS IN WATER

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A passive sampling technique based on permeation through a polymeric membrane has been used for collection of eight monocyclic aromatic priority pollutants from aqueous media. Pollutants permeating through the membrane are collected onto a solid adsorbent in the sampling device. Both solvent extraction and thermal desorption techniques were evaluated for the recovery of collected materials with quantification achieved by gas chromatography. Linear relationships between the amount of the pollutants collected and the product of exposure times and pollutant concentrations have been observed. The effects of the exposure temperature, pH, and the potential interferences were investigated. Sample species collected can be stored for three months without significant loss of the species.

*Keywords:* Priority Pollutants; permeation sampling; time-weighted-average concentration

## INTRODUCTION

Based on the Consent Decree obtained in Federal Court by public interest groups, the U.S. EPA has been directed to establish standards for a list of 65 "priority" pollutants (actually reflecting 129 individual compounds) to regulate discharges of these materials to the nation's waterway for the protection of both aquatic and human life[1]. Contained is a group of eight monocyclic aromatics, including 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene, nitrobenzene, 2,4-dinitrotoluene, and 2,6-dinitrotoluene. This group of compounds occurs in ambient water at the concentrations ranging from 1 ng/L to over 200 mg/L[2–5] The present method of collecting and analyzing these compounds approved by EPA[6] involves obtaining a grab water sample of 1 liter, transporting the sample to the laboratory, con-

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centrating it with methylene chloride extraction, and analyzing by GC-MS. The method suffers obvious drawbacks, such as long pretreatment time, a large amount of solvent being required which is eventually vented into the atmosphere, poor accuracy and precision as indicated by percentage recoveries from 55% to 79% for monocyclic aromatics.

Grab sampling only reflects the concentration of the pollutant at the time of sampling. Composite sampling and continual sampling with pumping and evacuation systems are able to produce time-weighted-average concentration when the concentration of the pollutant is expected to change with time. The former is labor-intensive while the later requires an external power source. Both can only be used for a relatively short time interval due to their limited capacities. In addition, the maximum holding time for most of the semivolatile organic compounds in water samples is 14 days at 4°C[7].

This paper describes a method for the collection, concentration, and determination of eight monocyclic aromatic priority pollutants in water. Passive sampling methods based on the permeation of species through a polymeric membrane and collection of permeants on an adsorbent were originally developed for personal monitoring of pollutants in air. It has been investigated for the sampling and determination of air pollutants[8–10], and for volatile organic species[11–13] and phenols[14] in water. Detection limits at the low µg/L level were readily attainable. Other researchers have also reported other membrane permeation samplers. Melcher and Morabito[15] developed an automated extraction analysis system using a silicone rubber tubing. Hexane was employed to extract chlorinated aromatics and pesticides which was then assayed by GC-ECD. This method, however, requires rigorous solvent flow control and field sampling is impossible. Lebo et al.[16] evaluated a passive method that employed segments of layflat polyethylene tubing with thin films of triolein sealed inside. It served as an *in situ* sampler of aqueous polychlorinated dibenzo-p-dioxins (PCCDs) and polychlorinated dibenzofurans (PCDFs). A 28-day sampling period was used to detect pg/L level of PCCDs and PCDFs. Compared with these methods, the sampler used in this paper has the advantages of simplicity, low cost, the ability to stabilize the sample and obtain time-weighted-average concentration over desired time. The applicability of the permeation sampler for eight monocyclic aromatic priority pollutants was studied. The calibration range of the permeation sampling device, the effect of the exposure temperature, pH, and the potential physical and chemical interferences, have been investigated. The preliminary field application of this sampler had been conducted using spiked water samples.

## EXPERIMENTAL

### Reagents

In all studies, reagent grade compounds were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI). Based on the solubilities of these compounds in water, stock solutions containing single compound with concentrations from 25 mg/L to 100 mg/L were prepared by dissolving in distilled water and chilled until use. Sample solutions were prepared by appropriate dilution. Due to its extremely low solubility in water (6 µg/L at 23°C)[4], saturated hexachlorobenzene water solution was prepared as the stock solution.

The membrane used in this study was a 0.038 mm thick silicone polycarbonate (Mempro Membrane Products Company, Troy, NY). Porapak Q adsorbent (50/80 mesh, Alltech Associates, Inc., Deerfield, IL) was washed with acetone and ethyl acetate, respectively, and thermally preconditioned at 225°C for 12 hours with nitrogen gas purge at 6 mL/min. Tenax-TA adsorbent (60/80 mesh, Alltech Associates, Inc., Deerfield, IL) was washed with acetone followed by thermal treatment at 300°C for 12 hours in a stream of nitrogen gas at 6 mL/min. Extraction with methanol and acetone was performed to clean other adsorbents evaluated in this study.

### Sampling and Analysis

The prototype permeation sampling device consists of a silicone polycarbonate membrane and a 70 mm long glass tubing with an inner diameter of 55.5 mm. The membrane was affixed to one end of the tubing with silicone rubber cement. A selected adsorbent, either 0.3g Porapak Q or 0.15 g Tenax-TA, was spread evenly on the inner surface of the sampling device which was then sealed with an aluminum foil-lined rubber stopper. The sampling devices were held by the cover of the exposure chamber and exposed to a monocyclic aromatic solution for a known period of time. After exposure, the adsorbent was transferred into a septum-capped vial and stored until analysis. Either solvent extraction with Porapak Q or thermal desorption with Tenax-TA was used to recover collected pollutants. The solvent extraction method was used to recover monocyclic aromatics in the mid- µg/L to mid- mg/L range, while thermal desorption was suitable for sampling low to mid- µg/L level pollutants.

A Hewlett Packard Model 5890 gas chromatograph with a flame ionization detector, a fused silica capillary column (HP-5, 15 m × 0.25 mm, 0.25 µm film thickness, Hewlett Packard), and a Hewlett Packard 3392A integrator was used for the separation and quantification of the monocyclic aromatics collected by Porapak Q. Monocyclic aromatics were extracted with 2 mL ethyl acetate in the sample vial for 10 minutes by mild shaking and a 1.0 μL aliquot was injected into the injection port and analyzed by gas chromatography.

Considering its insensitivity to water vapor and its outstanding thermal stability (up to 350°C)[17], Tenax-TA is the desirable adsorbent for thermal desorption. A thermal tube desorber, Model 850 (Environchem Inc., Kemblesville, PA) was connected to a Hewlett Packard 5890 gas chromatograph equipped with a HP-5 capillary column, a flame ionization detector, and a HP 3392A integrator. After exposure, the Tenax-TA was directly transferred to a thermal desorption tube (6 mm o.d. × 4 mm i.d. × 115 mm). The tube was then inserted into thermal desorption chamber and 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 the temperature of the transfer line was set at 250°C.

## RESULTS AND DISCUSSION

### Initial Membrane Evaluation

An initial membrane evaluation was conducted to examine the response time and determine the relationship between the response and exposure concentration. A flow-through permeation cell was used to evaluate the permeation behavior of monocyclic aromatic priority pollutants. The cell was constructed of stainless steel with an exposure area of 40.7 $cm^2$ and has been described previously[11]. Within the permeation cell, one side of the membrane was in continuous contact with an aqueous solution containing a single compound of known concentration at a flowrate of 5 mL/min, while helium was allowed to flow across the surface of the other side of the membrane at 10 mL/min. The helium flow was directed to a flame ionization detector (FID) of the gas chromatograph. The response of the FID was monitored over time until the response reached steady state. The maximum response obtained was then measured and plotted versus the concentration of the analyte (Figure 1), demonstrating a linear relationship. 2,4-dinitrotoluene and 2,6-dinitrotoluene quickly reached steady response in 6 and 8 minutes, respectively. For halogenated benzenes, the response time ranged from 40 minutes to 45 minutes. Nitrobenzene required 35 minutes to reach steady state.

### Evaluation of Adsorbent/Solvent System for Solvent Extraction

For the solvent extraction method, initial adsorbent studies were performed with various adsorbents, including Tenax-TA, Porapak Q, XAD-7, Chromosorb 103. In order to achieve maximum recovery for solvent extraction, ten organic solvents: chloroform, methylene chloride, carbon tetrachloride, ethanol, acetone,

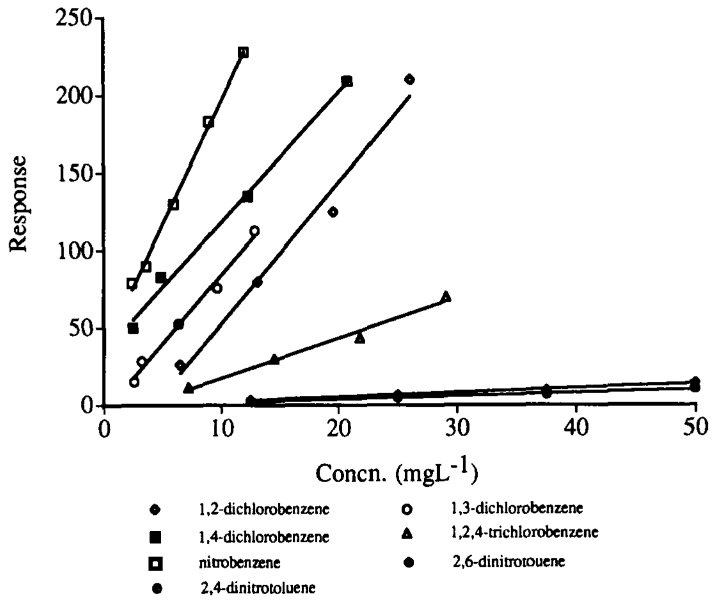

FIGURE 1 Overlay of Permeation Response Versus Concentration

acetonitrile, cyclohexane, ethyl ether, ethyl acetate, and benzene, were used to extract sample species from all the adsorbents evaluated. Table I shows the representative recovery results for 1,3-dichlorobenzene. It can be seen that ethyl acetate provides the highest recovery for most of the adsorbents. Similar results have been obtained for other compounds. The best adsorbent/solvent combination was then determined by further comparing the mass collected on each adsorbent using ethyl acetate as the solvent. The results indicated that Porapak Q was the optimum adsorbent.

## Evaluation of the Sampling Device

Previous studies on the permeation sampler have shown that a linear relationship exists between the mass of the analyte collected by the adsorbent and the product of external concentration and duration of exposure to the sampling device[11,14]. For a permeation sampler, provided that the adsorbent is an effective sink for the analytes, and its adsorption capability is not exceeded, vapor pressure on the adsorbent surface is zero. As a result, the permeation rate is directly proportional to the concentration of the external solution.

$$m = K\,(Ct) \qquad (1)$$

TABLE I Efficiency of Solvent Extraction for 1,3-Dichlorobenzene

| *Solvent* | *Relative Recovery (%)* | | | |
|---|---|---|---|---|
| | *Chromosorb103* | *Porapak Q* | *Tenax-TA* | *XAD-7* |
| chloroform | 0.97 | 0.77 | * | 0.86 |
| methylene chloride | 0.86 | 0.92 | * | 0.88 |
| carbon tetrachloride | 1.00 | 0.87 | * | 0.79 |
| methanol | 0.58 | 0.42 | 0.86 | 0.64 |
| acetone | 0.89 | 0.98 | 0.84 | 0.87 |
| acetonitrile | 0.96 | 0.73 | 0.86 | 1.00 |
| cyclohexane | 0.69 | 0.85 | 0.90 | 0.72 |
| ethyl ether | 0.79 | 0.78 | 0.75 | 0.59 |
| ethyl acetate | 0.98 | 1.00 | 1.00 | 0.85 |
| benzene | 1.00 | 0.87 | * | 0.91 |

*: Tenax-TA dissolves in benzene and chlorinated solvents.

K is permeation constant in $\mu g mg^{-1} L h^{-1}$, C is external concentration in mg/L, t is exposure time in hour, and m is mass collected in μg. In this way, it's possible to obtain time-weighted-average concentration of the compound in solution at any reasonable concentration and over any known period of time.

$$C = m/(Kt) \qquad (2)$$

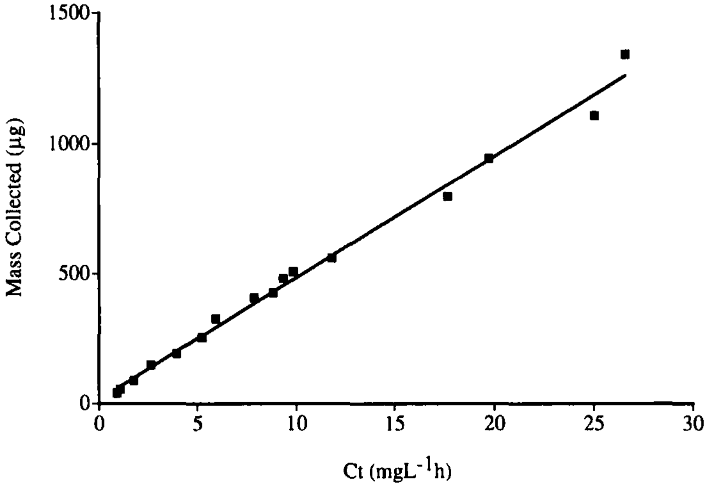

FIGURE 2 Calibration Curve of Solvent Desorption for 1,4-dichlorobenzene

To determine the permeation constants, the sampling device was exposed to the solutions of various known concentrations for from 2 to 36 hours. The pollutants collected by the adsorbent were recovered by either solvent extraction or thermal desorption and analyzed by GC-MS. The permeation constants for monocyclic aromatics were thus determined using equation 1. Since the aqueous solubility of hexachlorobenzene is extremely low, over 12 hour exposure was required to detect this compound by GC-MS. So the determination of its permeation constant was accomplished separately.

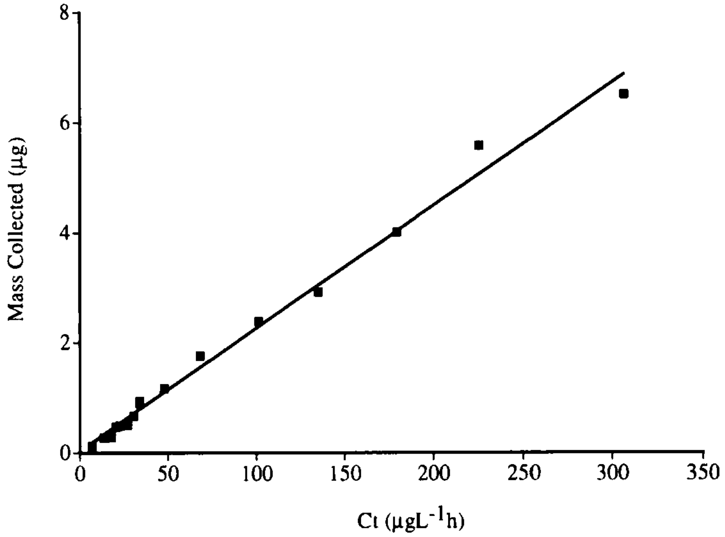

FIGURE 3 Calibration Curve of Thermal Desorption for 1,2,4-trichlorobenzene

Two sampling systems were evaluated using the prototype sampling device, i.e., Porapak Q absorption with solvent extraction of ethyl acetate, and Tenax-TA adsorption with thermal desorption. The typical calibration curves shown in Figures 2 and 3 indicate that the relationship between mass collected and the product of the exposure concentration and the exposure time is linear within the range investigated. The calibration results for passive sampler with solvent extraction are listed in Table II.

Thermal desorption was used to recover compounds with concentrations from low to mid- μg/L levels. Calibration results for all compounds are summarized in Table III. Due to its low solubility in water and very limited detection capability of FID, the exposure period of at least 24 hours is required for hexachlorobenzene. On the other hand, the inherent baseline noise of thermal desorption method makes it very difficult to identify the hexachlorobenzene. Thus, no further attempt has been made to recover hexachlorobenzene from water with passive sampling/thermal desorption.

TABLE II Calibration Results for Solvent Extraction with Porapak Q[*]

| *Compound* | *Exposure Range* $Ct\ (mgL^{-1}h)$[†] | *Concn. Range* $(mgL^{-1})$ | $K$[#] $(\mu g mg^{-1}Lh^{-1})$ | *Correlation Coefficient* |
|---|---|---|---|---|
| 1,2-dichlorobenzene | 0.860 – 32.6 | 0.132 – 16.3 | 52.8 ± 3.52 | 0.992 |
| 1,3-dichlorobenzene | 0.850 – 32.2 | 0.130 – 16.1 | 51.6 ± 2.80 | 0.993 |
| 1,4-dichlorobenzene | 0.898 – 26.6 | 0.150 – 13.3 | 49.7 ± 1.80 | 0.994 |
| 1,2,4-trichlorobenzene | 0.640 – 30.8 | 0.160 – 15.4 | 49.0 ± 2.72 | 0.990 |
| nitrobenzene | 0.789 – 25.3 | 0.121 – 12.7 | 44.3 ± 2.74 | 0.992 |
| hexachlorobenzene | 0.0864 - 0.300[‡] | 0.0003 – 0.006 | 174 ± 6.76 | 0.992 |
| 2,4-dinitrotoluene | 1.80 – 44.0 | 0.336 – 22.0 | 12.5 ± 0.580 | 0.996 |
| 2,6-dinitrotoluene | 1.23 – 41.4 | 0.254 – 20.7 | 21.5 ± 1.27 | 0.992 |

[*]: Exposure temperature 23°C, pH 7.
[†]: Exposure time: 2 – 36 hours.
[‡]: Exposure time: 12 – 48 hours, MS detector.
[#]: Confidence interval: 95%, t-test.

TABLE III Calibration Results for Thermal Desorption with Tenax-TA[*]

| *Compound* | *Exposure Range* $Ct\ (\mu gL^{-1}h)$[†] | *Concn. Range* $(\mu gL^{-1})$ | $K$[‡] $(\mu g\ \mu g^{-1}Lh^{-1})$ | *Correlation Coefficient* |
|---|---|---|---|---|
| 1,2-dichlorobenzene | 5.87 – 207 | 0.734 – 133 | 25.3 ± 3.13 | 0.990 |
| 1,3-dichlorobenzene | 5.79 – 298 | 0.725 – 149 | 19.2 ± 1.10 | 0.992 |
| 1,4-dichlorobenzene | 7.48 – 365 | 0.935 – 182 | 19.6 ± 1.58 | 0.984 |
| 1,2,4-trichlorobenzene | 5.81 – 307 | 0.726 – 153 | 22.3 ± 1.65 | 0.995 |
| nitrobenzene | 3.59 – 270 | 0.897 – 135 | 35.4 ± 2.89 | 0.991 |
| 2,4-dinitrotoluene | 7.76 – 362 | 0.970 – 181 | 13.8 ± 1.02 | 0.995 |
| 2,6-dinitrotoluene | 7.62 – 362 | 0.953 – 181 | 19.5 ± 1.08 | 0.992 |

[*]: Exposure Temperature 23°C, pH 7.
[†]: Exposure time: 2 – 10 hours.
[‡]: Confidence interval: 95%, t-test.

## Detection Limits, Precision and Accuracy

To determine the detection limits of monocyclic aromatics, the passive permeation samplers were exposed to a monocyclic aromatic solution with concentrations of approximately three to five times of the estimated detection limits for four hours at 23°C. Seven samples were collected, extracted with 1.5 mL ethyl acetate, and analyzed by gas chromatograph. The same procedure was performed with thermal desorption method. The detection limits for monocyclic aromatic priority pollutants are listed in Table IV. According to the EPA definition of detection limits[6], the results are reported with a 99% confidence interval. The detection limits can be further improved by prolonging sampling time and decreasing solvent volume for solvent extraction.

TABLE IV Detection Limit of the Passive Permeation Sampler*

| *Compound* | *Solvent Extraction*† *(mgL$^{-1}$)* | *Thermal Desorption*# *(μgL$^{-1}$)* |
|---|---|---|
| 1,2-dichlorobenzene | 0.110 | 0.692 |
| 1,3-dichlorobenzene | 0.0975 | 0.774 |
| 1,4-dichlorobenzene | 0.101 | 0.706 |
| 1,2,4-trichlorobenzene | 0.0910 | 0.686 |
| hexachlorobenzene | 0.0012‡ | --- |
| nitrobenzene | 0.0920 | 0.480 |
| 2,4-dinitrotoluene | 0.175 | 0.890 |
| 2,6-dinitrotoluene | 0.285 | 1.04 |

*: Exposure temperature 23°C, pH 7, confidence interval: 99%, t-test.
†: Exposure time 4 hours, solvent volume 1.5 mL.
‡: Exposure time 24 hours, solvent volume 1.0 mL, MS detector.
#: Exposure time 4 hours.

To evaluate the precision and accuracy, the sampling devices were exposed to a monocyclic aromatic solution for four hours at 23°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 concentration calculated from the calibration curve and the concentration spiked. Precision and accuracy results are given in Table V.

TABLE V Precision and Accuracy of Passive Permeation Sampler*

| *Compound* | *Solvent Extraction* | | | *Thermal Desorption* | | |
|---|---|---|---|---|---|---|
| | *Concn. (mgL$^{-1}$)* | *RSD (%)* | *Accuracy (%)* | *Concn. (μgL$^{-1}$)* | *RSD (%)* | *Accuracy (%)* |
| 1,2-dichlorobenzene | 1.09 | 2.9 | 94 | 6.90 | 7.2 | 90 |
| 1,3-dichlorobenzene | 1.07 | 3.9 | 94 | 6.78 | 5.3 | 105 |
| 1,4-dichlorobenzene | 1.10 | 1.6 | 106 | 6.95 | 5.8 | 108 |
| 1,2,4-trichlorobenzene | 0.808 | 2.6 | 98 | 5.12 | 7.4 | 98 |
| hexachlorobenzene | 0.006† | 4.2 | 92 | -- | -- | -- |
| nitrobenzene | 0.997 | 4.7 | 100 | 6.32 | 8.8 | 110 |
| 2,4-dinitrotoluene | 2.07 | 3.9 | 91 | 9.36 | 6.8 | 97 |
| 2,6-dinitrotoluene | 2.26 | 3.3 | 109 | 9.10 | 8.6 | 98 |

*: Exposure temperature 23°C, pH 7, exposure time 4 hours.
†: Exposure time 24 hours, MS detector.

## Storage Stability

To examine the storage stability of the monocyclic aromatics collected on Porapak Q and Tenax-TA, two sets of the samples were collected for both adsorbents. One set of the samples was chilled at about 4°C and another set was stored at room temperature in septum-capped vials. Adsorbent sample was extracted with ethyl acetate and analyzed at 5 day intervals. There is no obvious loss of collected species from either adsorbent for roomtemperature storage and refrigeration.

## Effect of Exposure Temperature

To determine the effect of the exposure temperature, the exposure chamber was immersed into a temperature controlled water bath. The study was performed over a range of from 3°C to 35°C, which covered the range of temperatures most likely found in ambient waters. Sampling devices were exposed at known temperatures for four hours and then analyzed by the method described previously.

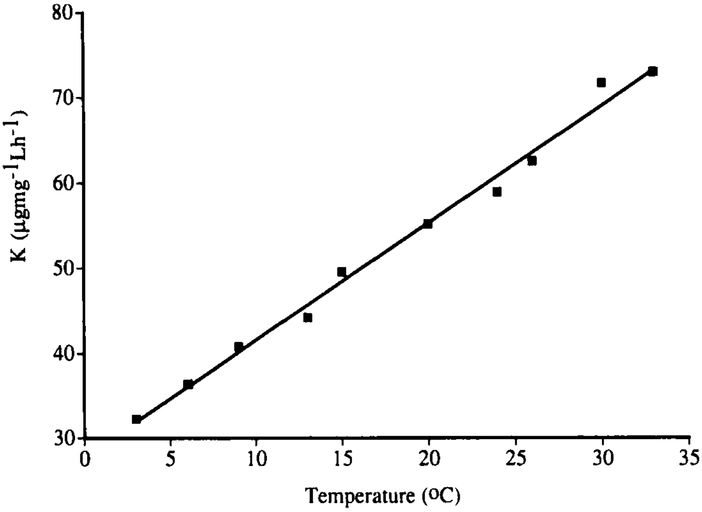

FIGURE 4 Effect of Exposure Temperature on Permeation Constant for 1,3-dichlorobenzene

It's been observed that for phenols, the increase of the permeation rate with respect to temperature in Celsius was nearly linear when the temperature changes within a relatively small range[14]. The results obtained for monocyclic aromatics confirmed that the linear relationship remains valid within the range examined (See Figure 4). Furthermore, when the sampling device is subjected to a temperature different from that of the calibration procedure (23°C), the permeation constant can be corrected by the following equation:

$$K_t = K + s\Delta t \quad (3)$$

where, $K_t$ is the permeation constant obtained at the average temperature over the sampling period, K is the permeation constant obtained at the calibration temperature, s which is calculated from the plot of $K_t$ versus t is the coefficient of the temperature effect (dK/°C), and $\Delta t$ is the temperature difference between the sampling temperature and the calibration temperature (°C). The percentage change of the permeation constant per degree is below 5% (See Table VI).

TABLE VI Effect of Exposure Temperature on Permeation Constants

| *Compound* | *s (dK/°C)* | *Percent Variation (%/°C)* |
|---|---|---|
| 1,2-dichlorobenzene | 1.4 | 2.8 |
| 1,3-dichlorobenzene | 1.4 | 2.7 |
| 1,4-dichlorobenzene | 1.4 | 2.8 |
| 1,2,4-trichlorobenzene | 1.4 | 2.9 |
| hexachlorobenzene | 4.3 | 2.5 |
| nitrobenzene | 1.0 | 2.2 |
| 2,4-dinitrotoluene | 0.49 | 4.2 |
| 2,6-dinitrotoluene | 0.82 | 3.7 |

## Effect of pH

To evaluate the effect of pH in ambient water on permeation response, sampling devices were exposed to monocyclic aromatic solutions at known pH ranging from 2 to 12. Phosphate buffers, hydrochloric acid, and sodium hydroxide were used to adjust pH. It was observed that pH has only a slight effect on the permeation rates of 2,4-dinitrotoluene and 2,6-dinitrotoluene when pH is below 4.5 and above 9.0. No change in response was observed for chlorinated benzenes and nitrobenzene.

## Potential Interference Study

The use of capillary column GC-MS should reduce or eliminate the potential interferences with the analytical finish. As a result, the potential interference species evaluated were compounds which could potentially block the permeation process, alter/coat the adsorbent, or change the forms of the analytes collected. Inorganic salts, detergent, and humic acid were examined. The inorganic chemicals used in this study included sodium chloride, sodium nitrate, sodium phosphate, sodium sulfate with concentrations up to 0.1 M. The sampling device was exposed to a solution containing one of the above chemicals and monocyclic aromatics at the concentration of 1 mg/L for 4 hours. The pH of the solution was adjusted to 7.0 prior to exposure. The inorganic species evaluated were found to have no significant effect.

Humic acid is the degradation product of organic matter, particularly dead plants and often found in ambient waters. It consists of a mixture of complex macromolecules having polymeric phenolic structures with the ability to chelate with metals[18]. The surface active agents from the residuals of detergents are found in wastewater stream at high frequency[19] that could affect the characteristic of the membrane as it lowers the surface tension of the aqueous solution. Sodium lauryl sulfate which has a solubility of 0,1g/mL in water[20] was used as a representative agent.

Humic acid was found to produce negative interference starting at concentrations above 0.1%. It's reported that humic acid is slightly soluble in water, usually with much swelling[18], but there is no available data regarding its aqueous solubility. It's possible that insoluble particles and swelled macromolecules might adsorb monocyclic aromatic molecules to some extent, thus decrease their concentrations in the solution. Sodium lauryl sulfate also caused a reduction in response when the concentration was above 0.10%. At these high concentrations, visible bubbles were observed to form on the surface of the membrane. Results for these studies are given in Figure 5.

## Analysis of Spiked Authentic Water Samples

To evaluate the performance of the permeation sampling device in an actual field sampling application, wastewater samples were obtained from local wastewater treatment plant where industrial and sewage wastewater was treated by an activated sludge process. The samples represented matrices of untreated raw influent and treated final effluent. Four sampling devices were exposed to each wastewater sample spiked with monocyclic aromatic compounds. Both the solvent extraction and thermal desorption methods were evaluated. The results are shown in Tables VIIa and b. Several parameters used to assay water quality are also listed in these tables. It can be seen that permeation sampling method with both solvent desorption and thermal desorption gives good analytical results in different matrices encountered in water sampling.

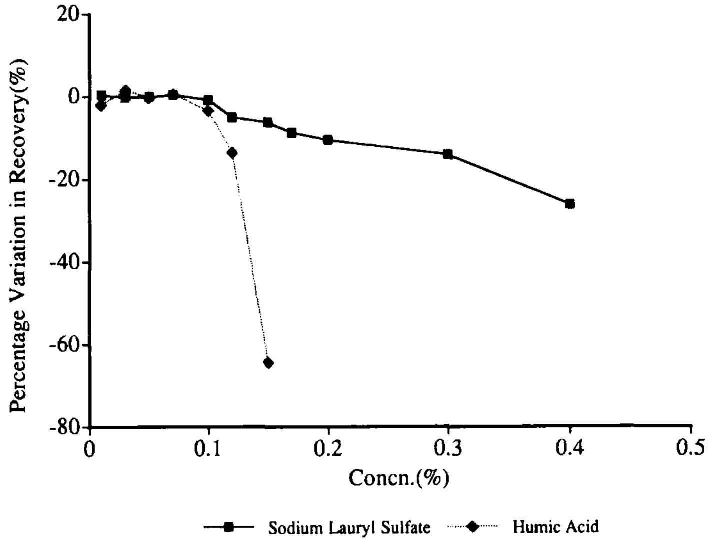

FIGURE 5 Percentage Variation in Recovery for 1,3-dichlorobenzene with Sodium Lauryl Sulfate and Humic Acid

TABLE VIIa Results of Spiked Authentic Wastewater Analysis Using Solvent Extraction*

| *Compound* | *Spiked Level ($mgL^{-1}$)* | *Raw Influent* | | *Final Effluent* | |
|---|---|---|---|---|---|
| | | *Recovered ($mgL^{-1}$)* | *Avg. Recovery (%)* | *Recovered ($mgL^{-1}$)* | *Avg. Recovery (%)* |
| 1,2-dichlorobenzene | 1.27 | 1.29 ± 0,15 | 102 | 1.38 ± 0.06 | 109 |
| 1,3-dichlorobenzene | 1.26 | 1.32 ± 0,14 | 105 | 1.33 ± 0.05 | 106 |
| 1,4-dichlorobenzene | 1.22 | 1.12 ± 0.1 | 92 | 1.14 ± 0.13 | 93 |
| 1,2,4-trichlorobenzene | 1.06 | 1.15 ± 0.14 | 108 | 1.03 ± 0.05 | 97 |
| hexachlorobenzene | 0.00282 | 0.00300 ± 0.00025 | 106 | 0.00273 ± 0.00025 | 97 |
| nitrobenzene | 1.17 | 1.15 ± 0.11 | 98 | 1.09 ± 0.06 | 93 |
| 2,4-dinitrotoluene | 1.22 | 1.13 ± 0.16 | 93 | 1.27 ± 0.11 | 104 |
| 2,6-dinitrotoluene | 1.22 | 1.18 ± 0.09 | 97 | 1.23 ± 0.14 | 101 |

TABLE VIIb Results of Spiked Authentic Wastewater Analysis Using Thermal Desorption*

| *Compound* | *Spiked Level ($\mu gL^{-1}$)* | *Raw Influent* | | *Final Effluent* | |
|---|---|---|---|---|---|
| | | *Recovered ($\mu gL^{-1}$)* | *Avg. Recovery (%)* | *Recovered ($\mu gL^{-1}$)* | *Avg. Recovery (%)* |
| 1,2-dichlorobenzene | 9.14 | 8.93 ± 0.88 | 98 | 8.43 ± 0.89 | 92 |
| 1,3-dichlorobenzene | 9.02 | 8.11 ± 0.93 | 90 | 8.67 ± 0.59 | 96 |
| 1,4-dichlorobenzene | 10.0 | 9.00 ± 0.93 | 90 | 9.62 ± 0.66 | 96 |
| 1,2,4-trichlorobenzene | 7.27 | 6.86 ± 0.64 | 94 | 6.98 ± 0.73 | 96 |
| nitrobenzene | 8.37 | 7.81 ± 0.86 | 93 | 8.36 ± 0.76 | 100 |
| 2,4-dinitrotoluene | 50.0 | 49.2 ± 6.4 | 98 | 53.9 ± 2.3 | 108 |
| 2,6-dinitrotoluene | 50.0 | 46.9 ± 6.9 | 94 | 45.6 ± 8.1 | 91 |
| *Additional Parameters* | | | | | |
| pH | | 6.5 | | 6.9 | |
| BOD-5 day (mg/L) | | 192 | | 4 | |
| COD (mg/L) | | 413 | | 38 | |
| TSS (mg/L) | | 328 | | 3 | |

*: Average of four replicate samplings, 95% confidence level.

## Summary

The permeation sampling method developed in this paper provides an alternative way for the sampling of monocyclic aromatic priority pollutants in water. It can eliminate many problems related to the current methods, such as complex devices, high cost, solvent venting, chilling and storage requirement for large volume of water samples, and tedious preconcentration steps. Owing to its unique feature of obtaining time-weighted-average concentrations of the pollutants, it can be used for the sampling and determination of water streams with pollutant concentrations changing over time. It's also possible to detect trace level pollutants by extending sampling time. The sampler is simple, light, inexpensive, and convenient for multilocation sampling.

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