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Continuous monitoring of volatile organic compounds in water using on-line membrane extraction and microtrap gas chromatography system

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Abstract

A method for continuous monitoring of volatile organic compounds (VOCs) in water is presented. The aqueous sample containing VOCs is passed through a hollow fiber membrane. The VOCs selectively migrate across the membrane into an inert gas stream. The VOCs are trapped and concentrated by a microtrap in front of the GC column. The retained VOCs are desorbed from the microtrap by an electrically generated temperature pulse. Rapid heating generates a concentration pulse of analytes which serves as an injection for chromatographic separation. Continuous monitoring is achieved by making a series of pulses (or injections) and corresponding to each pulse a chromatogram is obtained. This system showed excellent results for VOCs monitoring at trace levels. Detection limits for most VOCs were at the low ppb (μg/l) level.

1. Introduction

The list of volatile organic compounds (VOCs) includes a variety of alkyl substituted aromatic hydrocarbons, as well as organic molecules containing different functional groups. Presence of VOCs in water is a public health concern because many of the VOCs are toxic and/or carcinogenic. VOC contamination may be encountered in ground water, surface water, industrial waste water as well as in drinking water. VOCs may come from industrial spills and emissions, leachate from municipal and industrial landfills, and can be formed as byproducts of chlorination during the water treatment process. Federal regulations require monitoring of effluent streams for the presence of VOCs.

The conventional Environmental Protection Agency (EPA) approved method of collection and analysis of VOCs in water consists of obtaining a grab sample, transporting the sample to a laboratory and analyzing the sample by purge and trap (e.g., EPA 502.2, 602 methods). In purge and trap, the VOCs are purged from the aqueous sample by bubbling an inert gas through it. The inert gas carries the VOCs into a sorbent trap where they are retained. Then the VOCs are thermally desorbed from the trap and analysis is done by GC or GC–MS. Head space analysis is another popular method where the sample is first allowed to equilibrate in a sealed sample vial. Then a small head space sample is withdrawn

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and analyzed by GC or GC–MS. There are several inherent difficulties in the purge and trap procedure such as memory effect and incomplete desorption. The head space analysis has relatively poor accuracy and precision, and is usually used as a screening method. Direct injections of water samples have also been tried for analysis of VOCs, but the detection limits are usually quite high [1].

The limitation of the above mentioned techniques is that the sample has to be sent to the laboratory for analysis. These techniques can not be used for real-time, continuous monitoring. Real-time, on-line monitoring of VOCs in water offers several advantages. On-line techniques provide a more accurate analysis of VOCs by overcoming the problems associated with discrete sampling, sample preservation, transport, storage and laboratory handling of samples. Each of these steps may introduce errors such as sample loss and cross contamination. The grab samples are usually stable for a few days and the analysis has to be done within a few days. Very often samples have to be rejected just because the analysis could not be completed on time. Some of these problem can be solved using on-line monitoring techniques. Real-time VOC measurement devices can be used for continuous monitoring applications, such as monitoring ground water during clean up operations, drinking water supply, and waste water discharge from industries. Continuous monitoring can also be used in process control applications. Semicontinuous VOC monitoring systems for water have been developed based on purging of VOCs from water followed by IR or GC analysis [2]. At present there is a real need for a continuous monitoring technique which can separate and identify the different VOC components at trace level.

1.1. Membrane extraction of VOCs

In general, VOCs analysis in water involves an extraction/separation step where the VOCs are removed from the aqueous phase. The most common extraction method is purging with an inert gas as done in purge and trap. However, purging is a slow process and significantly increases the analysis time. The VOCs can be recovered from the aqueous phase via selective transport through a semi-permeable membrane. In this process, the aqueous sample is contacted with a membrane and the VOCs selectively permeate through the membrane into a gaseous phase on the other side. Membranes can be divided into two categories: nonporous and porous membranes. In nonporous membranes, the mechanism of VOCs permeation [3] involves the following steps. First the VOC components migrate from the aqueous phase to the surface of the membrane, and dissolve in the inside surface layer of membrane. Then the dissolved components migrate through the bulk membrane under a concentration gradient. This is followed by evaporation or stripping of the VOCs from the outer membrane surface into the stripping gas. On the contrary, in a microporous membrane (e.g. polypropylene membrane) the VOCs directly diffuse through pores. The nonporous, hydrophobic silicone membrane is more selective toward organic compounds, and it reduces the diffusion of water through the membrane. When the stripping gas is to be introduced directly into a GC column or GC–MS the elimination of water is an important consideration.

Measurement devices based on membrane separation have been developed for different type of applications [4–13]. VOCs from water sample have been directly introduced into mass spectrometers through a membrane without any GC separation [9–11]. An analysis system which combines membrane extraction followed by GC injection using a sampling valve has been reported [12,13]. Although gas sampling valves can automatically make injections into a GC column, they have certain limitations in trace analysis. Only a small volume (a few microliters to a milliliter) can be injected. A large injection causes excessive band broadening, while a small injection volume reduces sensitivity. As a result these systems have high detection limits and are not effective in monitoring at trace level.

1.2. On-line microtrap

The sample introduction device is the most important component in GC instrumentation

used for continuous, on-line monitoring. It should be able to make automatic, reproducible injections. Recently we have reported the development of an on-line microtrap (OLMT) for continuous monitoring of VOCs in air [14,15]. The microtrap is a short length of small diameter tubing containing an adsorbent. The microtrap is directly connected in front of the analytical column. A flowing gas stream containing the VOCs is introduced directly into a GC column through the OLMT. As the stream passes through the OLMT, the VOCs are retained by the adsorbent in the microtrap. A pulse of electric current rapidly heats the microtrap to desorb the trapped VOCs. Due to its low thermal mass, the microtrap can be heated (and cooled) very rapidly. This rapid desorption generates a concentration pulse of VOCs that serves as an injection for GC separation. So, the OLMT is not only an automatic injection device but also a sample preconcentrator. Consequently, low detection limits can be achieved using an OLMT.

In this investigation membrane extraction was combined with the on-line preconcentration cum injection by a microtrap. A membrane module consisting of a single hollow fiber membrane was used to extract the VOCs from the water sample into an inert gas stream. The VOCs in the gas stream were concentrated using an OLMT and then injected into GC for analysis. Continuous monitoring of the VOCs in water was achieved with this on-line membrane extraction microtrap system (OLMEM).

2. Experimental

The schematic diagram of the experimental system is shown in Fig. 1. Two different membrane module designs are possible using hollow fiber membrane: "flow-over" and "flow-through" [9,13]. In flow-through configuration, the aqueous sample is passed through a hollow fiber membrane while the stripping gas flows on the outside. While in flow-over configuration the water sample passes on the outside of the membrane. The membrane module here was operated in the "flow-through" configuration. The membrane used in this study was Dow Corning Silastic medical grade tubing (Dow Corning Corporation, Midland, MI, USA). The membrane size used was 0.012 in. I.D. × 0.025 in. O.D. (1 in. = 2.54 cm). The membrane module consisted of a single hollow fiber. The membrane was connected to narrow bore stainless steel

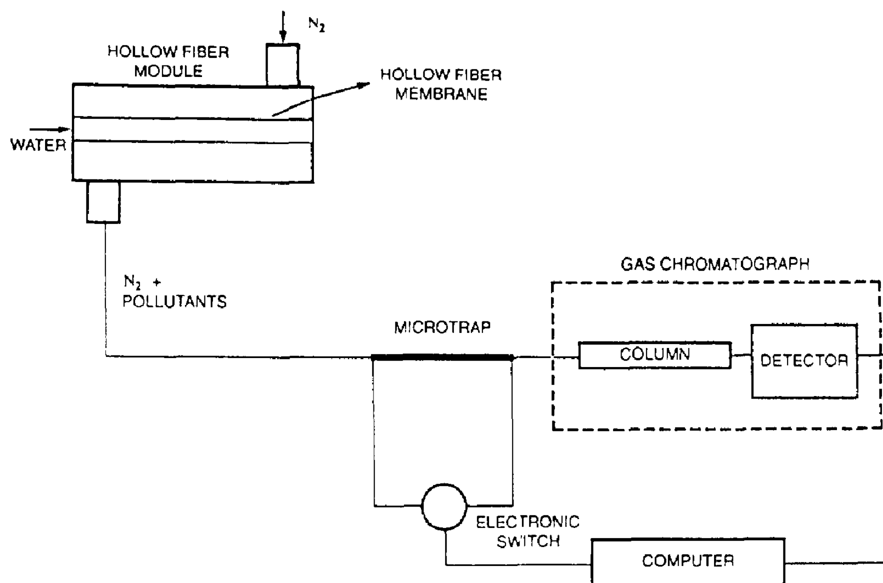

Fig. 1. Schematic diagram of the on-line membrane extraction microtrap system.

tubing of 0.015 inch outer diameter. To connect the hollow fiber membrane to the steel tubing, the end of the membrane was immersed in xylene for about 5 minutes. When it became swollen, 2 cm of the membrane was carefully slipped over the tubing. After the solvent evaporated, the membrane shrank to form a tight fit. The connection point was sealed by silicone glue. The active length of the fiber was approximately 20 cm.

A Hewlett-Packard 5890 Series II gas chromatograph (Hewlett Packard Company, Avondale, PA, USA) equipped with a conventional flame ionization detector was used for analysis. A 30 m long DB-1 fused-silica open-tubular column from J and W Scientific (Folsom, CA, USA) was used. The column inner diameter was 0.25 mm, and the stationary phase thickness was 1.0 μm. Typical flow rates were between 2 and 6 ml/min and the oven temperature was 95°C.

The microtrap was made by packing a length of 0.52 mm I.D. silica-lined stainless steel tubing with 60 mesh (0.25 mm) Carbotrap C. This microtrap had a resistance of 0.1 Ω/cm and its length was 14 cm. The microtrap was connected to a variable power supply (20–50 V AC). A computer-controlled electric switch was used to control the interval between pulses and also the time for which the microtrap current was turned on. Power resistors were put in series with the microtrap to limit the current through it. More detail of the microtrap and its operation are presented elsewhere [15].

2.1. System operation

The aqueous sample was pumped through the membrane module using an HPLC pump (Altex, Model 110A). Nitrogen (stripping gas) flowed counter-current around the membrane fiber and carried the permeated VOCs to the microtrap. The microtrap was pulsed (or heated) at regular intervals, and corresponding to each pulse a chromatogram was obtained. Interval between pulses were anywhere from a few seconds to several minutes. In a typical operation the microtrap was heated with a 5–10 A current for a duration of 500 to 1500 ms. All transfer lines were heated to 100°C to prevent any condensation of VOCs.

3. Results and discussion

The operation of the analytical system is demonstrated in Fig. 2 where a water stream containing 87 ppb (μg/l) each of benzene, toluene and ethyl benzene was continuously monitored. The water flowed continuously through the membrane module. Microtrap pulses were made at fixed intervals of time, and corresponding to each injection a chromatogram of the three compounds was obtained. In this example, analysis was done every two minutes. Excellent reproducibility of peak height, peak shape as well as retention time was obtained. For twenty-one consecutive injections, the relatively standard deviations of peak area for benzene, toluene and ethyl benzene were 1.4%, 0.41% and 0.44% respectively. In fact the relative standard deviation was lower than that obtained by making direct injections using a conventional GC injection port (R.S.D. was 2%). This shows that not only the microtrap injections, but also the membrane extraction process was quite reproducible. The heating–cooling cycle of the microtrap is very short (less than 5 seconds) and it is capable of making injections every few seconds. How often injections can be made depends upon the time required for GC analysis. Hence, it is advantageous to reduce the separation time as much as possible.

As mentioned before, the microtrap acts as a sample concentrator. It accumulates VOCs during the interval between two pulses (referred to as a pulse interval). So, the longer the interval, the greater is the amount of VOCs accumulated and larger is the detector response to a microtrap pulse. A typical detector response as a function of pulse interval is presented in Fig. 3. It is observed that as the time period increases, the response of the microtrap increases linearly until a maximum value is reached beyond which the response stays constant. The microtrap response can not be indefinitely increased because the

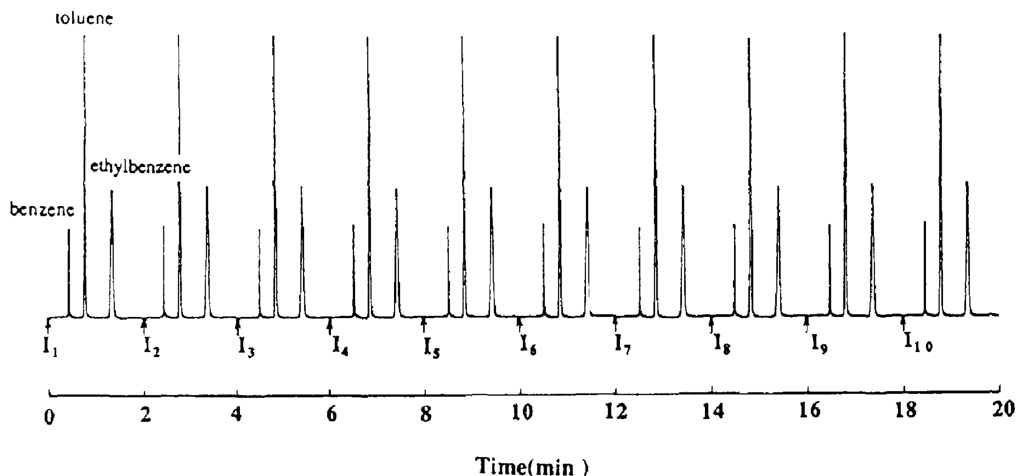

Fig. 2. Continuous monitoring of a water stream containing 87 ppb each of benzene, toluene and ethyl benzene. Microtrap pulses were made every two minutes at point I_1, I_2, I_3 . . . . Water flow rate was 1 ml/min, column temperature was 95°C, flow rate of stripping gas was 2 ml/min and temperature of membrane module was 80°C.

microtrap contains a small amount of adsorbent, and can retain the sample only for a short period of time before the sample breaks through. The analysis can be carried out quantitatively in the linear region or in the flat part of Fig. 3 [15].

3.1. *Quantitative aspects of the analytical system*

The calibration curves for several VOCs are presented in Fig. 4. The linear relationship between system response and concentration was

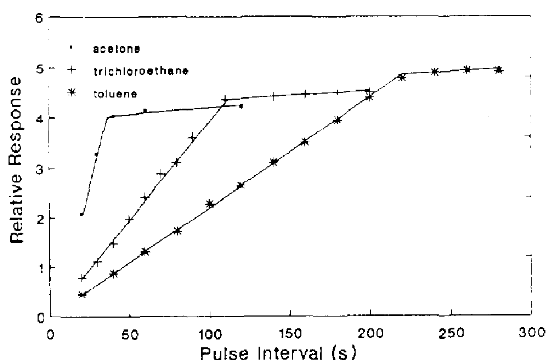

Fig. 3. Response of the analytical system as a function of interval between microtrap pulses. Water flow rate was 1 ml/min, flow rate of stripping gas was 5 ml/min, temperature of membrane module was 80°C.

observed in the low ppb to high ppm (mg/l) range. Detection limits (at signal to noise ratio of 3 [16]) for some VOCs is presented in Table 1. It is seen that this system showed low detection limits. For example, the detection limits for trichloroethane using this system was 0.28 ppb as compared to 30 ppb when a cryogenically cooled gas sampling value was used in another study [12]. The non-polar, hydrophobic molecules showed a detection limits in the low ppb levels, whereas the detection limit for the water soluble compounds such as acetone and ethanol was considerably higher.

The detection limit depends upon the extraction efficiency of the membrane as well as the preconcentration effect of the microtrap. By increasing the pulse interval, more analyte can be accumulated in the microtrap and consequently the detection limit can be lowered. The detection limits presented in Table 1 correspond to a pulse interval of 2 min. Detection limit could also be reduced by subambient cooling of the microtrap [15]. However, for a continuous monitoring device, subambient cooling is expensive and cumbersome, and was avoided in this application. It may be possible to further lower the detection limits by redesigning the membrane module with a longer hollow fiber or using

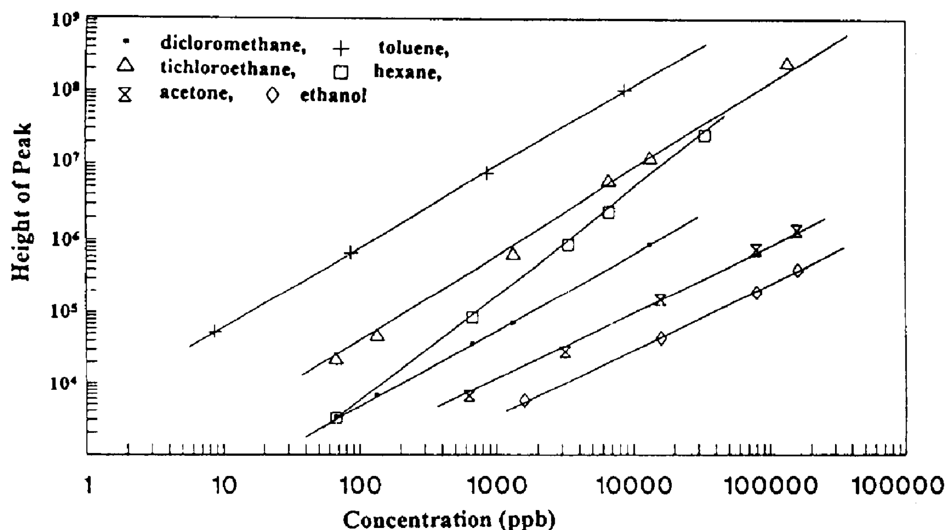

Fig. 4. Calibration curve for different VOCs. Water sample flow rate was 1 ml/min, pulse interval was 2 min, flow rate of stripping gas was 2 ml/min, membrane module was 80 C and column temperature was 70°C.

multiple hollow fibers so that higher extraction efficiency can be obtained.

The membrane extraction efficiency may be expressed as enrichment factor [4], E:

$$E = \frac{\text{mole fraction of analyte in stripping gas}}{\text{mole fraction of analyte in aqueous solution}}$$

The enrichment factor was experimentally determined by measuring the concentration of the VOCs at the inlet and the outlet of the membrane module and results are presented in Table 1. The enrichment factor was seen to vary between 4.1 and 65.1. As expected, the compounds with low enrichment factor have high detection limits, e.g., acetone and ethanol.

The membrane extraction process is analogous to liquid–liquid extraction and the partition coefficient of the VOCs between the membrane and aqueous phase determines the enrichment factor. Experimental values of the partition coefficient between the membrane and the aqueous phase are not available. So, the partition coefficients for these VOCs in the hexane–water

Table 1
Detection limits and enrichment factors for different VOCs

Compound	Detection limit (ppb) [a]	Enrichment factor [b]	Partition coefficient [17]	
			$\log P_{\text{octanol}}$	$\log P_{\text{hexane}}$
Toluene	0.042	65.1	2.11	2.85
Trichloroethane	0.28	61.8	2.31	NA [c]
Hexane	1.45	44.1	1.88	NA
Dichloromethane	7.75	42.4	1.68	NA
Acetone	61.1	7.5	−0.24	−0.92
Ethanol	212	4.1	−0.32	−2.26

The temperature of the membrane module was 80°C and the water flow rate was 1 ml/min.
[a] Pulse interval was 2 min.
[b] Water samples were analyzed by direct GC injection.
[c] NA = not available.

and octanol–water system [17] are listed in Table 1. Partition coefficient into the silicone membrane has been reported to be somewhat similar to the hexane–water system [5]. A correlation between enrichment factor and partition coefficient, and an inverse relation between partition coefficient and detection limits were seen. For example, acetone and ethanol have low partition coefficients, low enrichment factors, and high detection limits.

3.2. Optimization of membrane extraction conditions

To achieve high sensitivity it is desirable to transport as much of the VOCs as possible through the membrane into the GC. Two mechanisms control the transport of VOCs: (1) diffusion through the membrane; (2) mass transfer in the aqueous phase. The diffusion of VOCs through a membrane is governed by Fick's law of diffusion [18]. At steady state, the rate of diffusion per unit surface area per unit time is given as F:

$$F = -D \partial C / \partial X \quad (1)$$

where D is the diffusion coefficient of the VOCs in the polymeric membrane, and $\partial C/\partial X$ is the concentration gradient across the membrane. For a hollow fiber membrane:

$$\partial C / \partial X = (C - K_1 C_0) / L \quad (2)$$

where K_1 is the partition coefficient between the membrane and the aqueous phase, C_0 is the concentration of VOCs in aqueous phase, C is the concentration of VOCs on outside surface of membrane and L is the membrane thickness.

When the flow rate of the stripping gas is high enough, C is close to zero. $K_1 C_0$ represents the concentration of the analyte on the inside membrane surface which is in contact with the aqueous sample. Under these conditions:

$$F = D K_1 C_0 / L \quad (3)$$

According to this equation, F depends upon D and K_1 which in turn depend upon temperature. Thus, the temperature of the membrane module is an important factor which will effect the system response.

The flow rate of aqueous phase in the membrane is another important factor because the mass transfer in the aqueous phase depends largely upon it. The inorganic salt concentration (or ionic strength) and pH of the water sample are other parameters which can effect the system response.

Effect of flow rate

The effects of sample flow rate on the detector responses for dichloromethane and hexane at two different temperatures are shown in Fig. 5. As flow rate is increased, the system response increases because at higher flow rate there is more mixing at the water–membrane interface, and the formation of a boundary layer is reduced or eliminated. At higher flow rates, the rate limiting step is the mass transfer through the membrane rather than migration of the analyte through aqueous phase. Thus, increasing the flow rate beyond a certain value has negligible effect on system response.

For the components that permeate rapidly through the membrane, mass transfer in the aqueous phase is the rate limiting step. Mass transfer is better in a turbulent flow rather than in a laminar flow. Laminar flow turns turbulent at a Reynolds number between 2000 and 3000

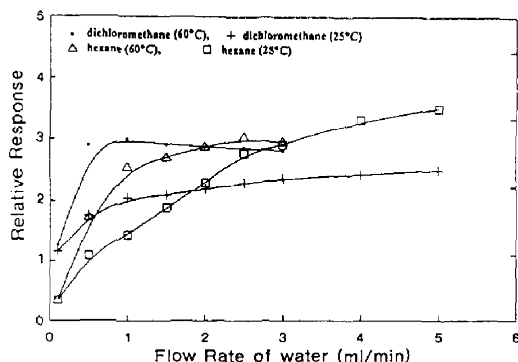

Fig. 5. Response of analytical system as a function of flow rate of water. Pulse interval was 2 min, flow rate of stripping gas was 2 ml/min and temperature of membrane module was 80°C.

[19]. The Reynolds number is calculated using the equation

$$N_{Re} = v\ d\ \rho/\mu \quad (4)$$

Here, d is the inner diameter of the membrane, v is the linear velocity of water stream, ρ is the density of the water stream, and μ is the viscosity of water stream. The membrane used here has an inner diameter of 0.012 in. and the N_{Re} reaches 2500 at a flow rate of 38 ml/min. At such a high flow rate, there is significant pressure drop across the narrow diameter hollow fiber. The silicone fibers are relatively delicate and are unable to withstand such pressure drops and can easily tear, especially at the connections. Another problem at high flow rate is that the residence time is short and only a small fraction of the analyte is extracted from the sample stream. To increase turbulence without increasing flow rate, the membrane tubing can be packed with glass beads [20]. However this method may increase the memory effect of the membrane module and will be addressed in future studies.

Effect of temperature

The effect of the water temperature on the system response is shown Fig. 6. It was seen that the responses initially increased with the increase in temperature. Beyond a temperature of 60°C for dichloromethane and 80°C for trichloroethane and chloroform, the responses decreased with increase in temperature. So, when response was plotted as a function of temperature the curve passed through a maximum point. The maximum point for all the compounds with the exception of acetone was in the temperature range studied here. The reason for such behavior is that permeability is a function of rate of diffusion (F) as well as the solubility of the analyte in the membrane [18,21]. The diffusion coefficient D increases with temperature and an Arrhenius type relationship exists:

$$D = D_o \exp(-E_d/RT) \quad (5)$$

where D_o is the diffusion coefficient at reference temperature, T is temperature and E_d is the activation energy for diffusion. However, solubility of the organic analyte in the membrane decreases with increase in temperature:

$$S = S_o \exp(-\Delta H/RT) \quad (6)$$

where ΔH is the apparent heat of solution, which has a negative value for organic liquid.

The initial increase of system response with increasing in temperature is due to the increased rate of diffusion. However, as temperature is further increased the decrease in solubility becomes the dominant factor and the system response begins to decrease.

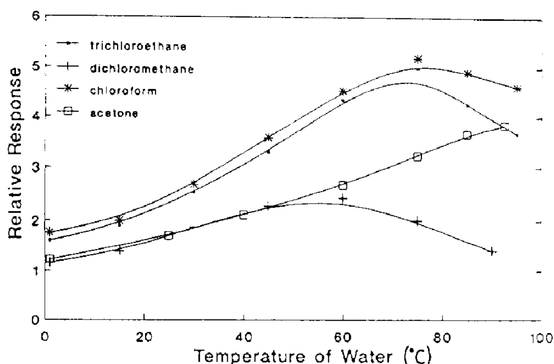

Fig. 6. Response of analytical system as a function of water temperature. Sample flow rate was 1 ml/min. Pulse interval was 2 min. Flow rate of stripping gas was 2 ml/min. Column temperature was 70°.

Effects of salinity

Environmental samples may contain inorganic ions such as Na^+, K^+, Cl^- etc. For example, in typical surface water and ground water, the total ionic strength may be of the order of 0.01 mol/l and 0.05 mol/l respectively, whereas in sea water the ionic concentration may be as high as 0.5 mol/l. The effect of ionic strength on the system response was studied in the concentration range of 0.0 to 4.0 mol/l using NaCl. The effect of salinity on ethanol, acetone, toluene and dichloromethane are shown in Fig. 7. In the low concentration range (0–0.4 mol/l), the response was unaffected by salt concentration. However, at higher concentrations (NaCl > 0.4 mol/l), the responses of toluene and dichloromethane de-

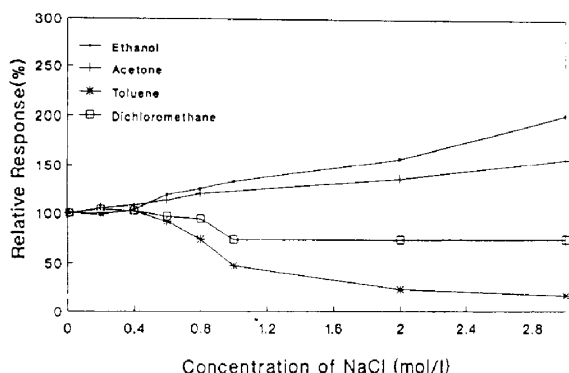

Fig. 7. Effect of ionic strength on system response for different VOCs. The sample response of zero ionic strength is considered 100%. The concentrations of toluene and dichloromethane were 1 ppm and the concentrations of acetone and ethanol 5 ppm.

creased with the increase of sodium chloride concentration, but the responses of acetone and ethanol increased with the increase of sodium chloride concentration. It seems that high ionic strength solutions, each component behaves differently. From a practical point of view, one seldom encounters ionic strength greater than 0.1 mol/l where the system response is not a function of ionic strength. At higher ionic strength recalibration of the system would be necessary.

Effect of pH

Usually the pH of environmental samples are in the range of 2.5 to 10.5. The response of two test compounds, toluene and ethanol, was studied in the pH range of 1.5 and 12.5. Both these compounds did not show any significant variation in response with pH. This is expected for most VOCs although pH may turn out to be an important factor for organic compounds that are acidic or basic [5].

4. Conclusion

The on-line membrane extraction microtrap system can be used to provide continuous, on-line monitoring of VOCs in water samples at ppb level. The microtrap is effective as an automatic, on-line, sample preconcentrator cum injector. As a result, the detection limits for most of VOCs were at the low ppb level. The detection limits for the water soluble, polar compounds was relatively higher than the nonpolar ones.

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