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Continuous monitoring of volatile organic compounds in air emissions using an on-line membrane extraction–microtrap–gas chromatographic system

Somenath Mitra*, Naihong Zhu, Xin Zhang, Barbara Kebbekus

Department of Chemical Engineering, Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ 07102, USA

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Abstract

A method for the continuous monitoring of volatile organic compounds (VOCs) in air using on-line membrane extraction followed by gas chromatographic analysis is presented. The air is passed through one or more hollow-fiber membranes and the VOCs selectively permeate across the membrane into a flow of inert gas such as nitrogen. Before entering the GC column, the VOCs are trapped and concentrated by a microtrap. A concentration pulse of the trapped VOCs is generated by direct electrical heating of the microtrap, which serves as injection for GC separation. Continuous monitoring is done by making injections at fixed intervals of time while the air stream flows continuously through the membrane module.

Keywords: Membrane extraction microtrap; Volatile organic compounds

1. Introduction

The detection and quantitative measurement of volatile organic compounds (VOCs) at trace levels in air emissions is of considerable importance because they are hazardous to public health and cause ozone formation in the troposphere. The development of rapid and sensitive analytical instrumentation is necessary to monitor the ambient VOCs in the environment and to monitor emission sources. Traditional methods to analyze for VOCs in ambient air and stack emissions use either whole air samplers such as Tedlar bags and canisters or sorbent cartridges [1]. In either case, the sample is collected in the field and the analysis is done in the laboratory. Consequently, there may be a significant delay between sampling and analysis. Also, there may be inaccuracies associated with sampling, sample transport and storage. Moreover, most of these techniques require extensive sample handling, which increases the analysis cost per sample.

For process environmental monitoring and process control, the analytical results are critical and the information is needed as soon as possible. Hence, there is a real need for instrumentation that can be used to carry out auto-

* Corresponding author.

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mated, on-line analysis to provide information on a continuous basis that can be used for process control and for meeting regulatory compliance. Techniques such as mass and FTIR spectrometry are being used for on-line monitoring and their merits and disadvantages have been discussed [2–4]. Gas chromatography (GC) is particularly attractive for monitoring VOCs because of its separation capability. Also, a variety of sensitive and selective detectors including MS and FTIR are available for GC.

The objective of this work was to develop a GC-based system for continuous monitoring of VOCs in air emissions. Most emission streams are complex mixtures and along with VOCs contain large amounts of other components. For example, combustion sources contain large amounts of water vapor, CO_2, SO_2, NO_x, etc. Some of these background gases may interfere with VOCs determination and need to be removed before analysis. Here, the VOCs are allowed to permeate selectively through a membrane into an inert gas, then the permeated VOCs are concentrated and injected into a gas chromatograph using a very small sorbent trap referred to as a microtrap.

1.1. Membrane extraction of VOCs

In the last few years, membrane separations have been used in a variety of applications such as gas separation and dehumidification, osmosis, reverse osmoses, ultrafiltration, dialysis and electrodialysis. Several analytical applications of membranes have also been reported [5–8]. Membrane interfaces for mass spectrometry have received the most attention and several commercial instruments based on this principle are currently available [4,9].

Membranes may be classified as "porous" where separation occurs by selective diffusion through small pores, or "non-porous" where the analyte permeates through a polymeric membrane by an activated diffusion process. In this study, a non-porous membrane was used. The mechanism of non-porous permeation membranes is a combination of solubility and molecular diffusion. First the analytes dissolve in the polymeric material and then diffuse through it under a partial pressure (or concentration) gradient. Barrer [10] and others [11,12] showed that diffusion is usually the rate-controlling step in the permeation process. Diffusion of an analyte in a membrane can be described by Fick's first law, which takes the following form for one-dimensional transport in a direction normal to the membrane interface:

$$J = -D(\partial C/\partial X)$$

where J is the rate of diffusion of the permeant gas through a unit reference area, D is the diffusion coefficient for a specific permeant–membrane system at a certain temperature, and C is the concentration of the permeant in the membrane at a position coordinate X. The concentration gradient can be obtained from Fick's second law:

$$\partial C/\partial t = \partial(D\ \partial C/\partial X)/\partial X$$

where $\partial C/\partial t$ is the rate of change of concentration with time, t, at a position coordinate X.

Since hollow fibers provide large surface-to-volume ratios and high packing densities, hollow-fiber membranes were selected to make the membrane module. Permeation through a tubular membrane can be expressed as follows:

$$G = P_0 2h(p_p - p_f)/\ln(r_o/r_i)$$

where G is the total rate of gas permeation, h is the length of the hollow fiber, P_0 is permeability coefficient, p_p and p_f are the permeant partial pressures at the permeate side and the feed side of the membrane, respectively, and r_i and r_o are the inner and outer radii of the tube, respectively.

1.2. On-line microtrap

The concentration of VOCs in air emissions and consequently in the permeate stream can be low, at the ppt to ppm level. Hence it is necessary to concentrate the analytes from a large volume prior to GC analysis. Direct injection of large samples into a GC system is not possible because of excessive band broadening. Here, an on-line microtrap is used for sample preconcen-

tration and injection. Trace analytical applications using the microtrap have been reported previously [13–15].

The microtrap is made by packing a small-diameter tube with an adsorbent. It is placed at the entrance to the GC column instead of the injector. The N_2 stream containing the VOCs passes through it. The analytes are trapped by the adsorbent while the N_2 serves as the carrier gas. The microtrap can be electrically heated with a pulse of electric current so that the analytes desorb as a concentration pulse sharp enough to serve as an injection for GC separation. The system operation involves heating the microtrap at regular intervals of time, and corresponding to each injection a chromatogram is obtained. Owing to its small size and low heat capacity, the microtrap can be heated/cooled rapidly, and injection can be made every few seconds. The electric pulses are controlled by a computer.

2. Experimental

The experimental system consists of the membrane module, the microtrap and a GC–flame ionization detection (FID) system. The overall set-up used for the experiment is presented in Fig. 1. The air sample flowed through the membrane module, inside the membrane fibers. Nitrogen (stripping gas) flowed countercurrent around the membrane fibers and carried the permeated VOCs from the membrane module to the GC column. Before entering the GC column, the VOCs were trapped by the microtrap. The microtrap was heated (or pulsed) at regular intervals. A chromatogram was obtained for each pulse.

The membrane module was constructed from a piece of 1/4-in. tubing with as many as 20 hollow fibers going through it. A silicone membrane consisting of a polydimethylsiloxane elastomer, purchased from Dow Corning, was used throughout. It is chemically, physically and thermally stable, with a size of 0.012 in. I.D. and 0.025 in. O.D. and an active length of the fibers anywhere between 3 and 20 cm.

The microtrap was made by packing a 0.53 mm I.D. deactivated fused-silica-lined stainless-steel tube with Carbotrap C (Supelco, Bellefonte, PA, USA). The length of the microtrap was about 14 cm. A current of 7–10 A was used to heat the microtrap. The energy was supplied by a Variac (STACO Energy Products) and the switching was done using a microprocessor-controlled device built in-house. The heating current to the microtrap could be turned on for a prespecified duration and at a fixed interval of time. Current pulses were applied anywhere between 30 s and 3

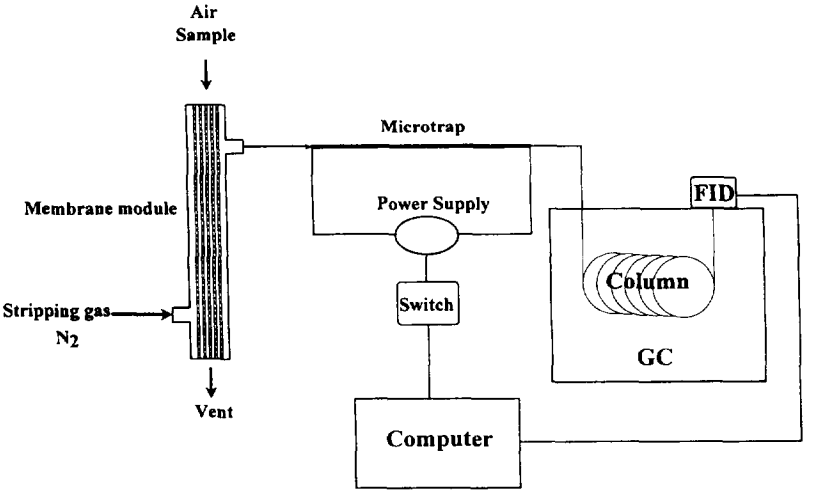

Fig. 1. On-line membrane extraction–microtrap–GC system.

min and the duration of each current pulse was between 0.5 and 1.5 s. Since the microtrap operation is fast and conventional thermocouples have short response times, it is not possible to measure the microtrap temperature accurately. A crude measurement using a thermocouple showed that a temperature as high as 300°C was reached in 1–2 s.

A Varian Model 3400 gas chromatograph equipped with a flame ionization detector was used. A 30 m × 0.315 mm I.D. DB-624 column (J&W Scientific, Folsom, CA, USA) with a 1.8-μm thick stationary phase layer was used for separation. The GC injection port was bypassed and the sample was introduced directly into the column through the microtrap.

All the chemicals used were of chromatographic grade. Certified gas standards were obtained from Alphagaz (Morrisville, PA, USA). Different concentrations of sample were also prepared in the laboratory in a canister or in a small gas cylinder. In some experiments, diffusion tubes were used to generate a VOCs stream using the method published by Savitzky and Siggia [16].

3. Results and discussion

3.1. Performance of the monitoring system

The operation of the analytical system was demonstrated by continuously monitoring a standard gas mixture whose composition simulated the emission from a hazardous waste incineration. It contained 1 ppm each of benzene, toluene, ethylbenzene and trichloroethylene (TCE) along with combustion products such as CO_2, CO and SO_2. To study the effect of moisture, humidified samples were used. The standard gas flowed continuously through the membrane module at a flow rate of 15 ml/min and the microtrap was pulsed every 3 min. A chromatogram of the four compounds was obtained each time a pulse was made (Fig. 2). From Fig. 2, it was observed that good precision of

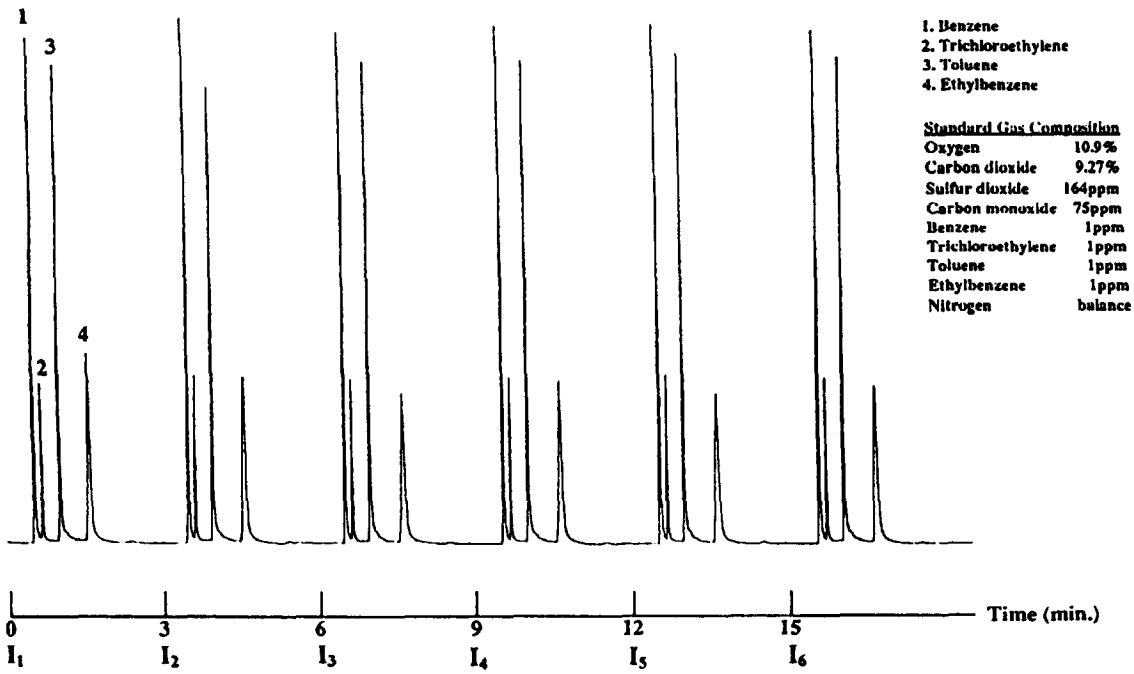

Fig. 2. Continuous monitoring of simulated stack gas. I_1–I_6 are the injections corresponding to which the chromatograms are obtained.

peak height, peak shape and retention time was obtained. Thus the membrane extraction process, the microtrap injections and their combination were all reproducible. The factor that limits the frequency of analysis is the column separation time rather than the heating–cooling cycle of the microtrap, so it is advantageous to shorten the separation time if analyses are to be performed more frequently.

The calibration graphs for several VOCs for the membrane extraction–microtrap–GC system are presented in Fig. 3. A linear relationship between system response and VOCs concentration was observed in the low to high ppm range. This result showed that the membrane permeation process and the retention process in the microtrap were linear. The samples used here were TCE, ethyl benzene and toluene.

Detection limits [17], measured as the signal-to-noise ratio, for toluene and ethylbenzene were 5.7 and 10.8 ppb, respectively. In general, low detection limits (ppb level) were achieved with this analytical system. However, as will be seen later, the system response and, consequently, the detection limit depends on the operating parameters and also the designs of the membrane module and the microtrap. The above values were obtained using a membrane module containing only one fiber and analyses performed every 3 min. It could be further lowered by using a membrane module containing a larger number of fibers and/or changing some other operating parameters.

3.2. Effect of pressure differential

A permeation process can be spontaneous only if the chemical potential change of the permeant is negative. For a permeant–membrane system, the chemical potential change across the membrane from the feed side to the permeate side can be expressed as follows [18]:

$$\mu_{ip} - \mu_{if} = RT \ln(P_{ip}/P_{if})$$

where P_{ip} is the partial pressure of analyte i in the permeate side of membrane and P_{if} is the partial pressure of i in the feed side. When the partial pressure of the feed side of the membrane

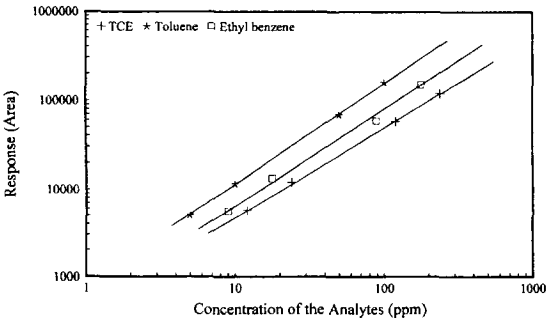

Fig. 3. Calibration graphs for (+) TCE, (*) toluene and (□) ethylbenzene.

is greater than the permeate side of the membrane, $P_{ip} < P_{if}$, $\ln(P_{ip}/P_{if})$ negative, the permeation process occurs spontaneously. In this case, the pressure difference (or the fugacity difference) offers the driving force needed for the mass transfer through the membrane.

The effect of the pressure differential on the response of the system was investigated. Experiments were carried out with benzene, toluene, TCE and ethylbenzene. The partial pressure gradient was provided by maintaining a pressure differential between the feed and permeate sides. The results are presented in Fig. 4. It was observed that the response of the system increased with increasing pressure differential between the feed and carry gas sides of membrane and the response increased sharply when the pressure difference was more than 45 p.s.i. In this experimental system, the pressure in the per-

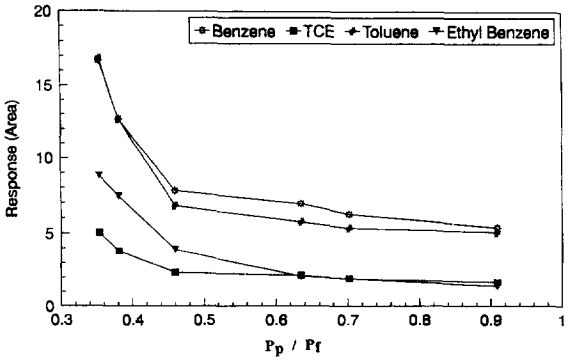

Fig. 4. Effect of pressure differential on the system response. P_p is the pressure on the permeate side and P_f that on the feed side of the membrane.

meate side of the membrane usually cannot be too low because a positive pressure is needed in GC to push the sample through the analytical column. On the other hand, the silicone membranes are relatively delicate and are unable to withstand elevated pressures on the feed side. Therefore, the key to efficient operation is the maintenance of an optimum pressure differential without jeopardizing GC operation or destroying the membrane.

3.3. Effect of sample air flow-rate

Flow-rate is an important parameter that determines the system response. The effect of varying the flow-rate of the air stream on the system response is shown in Fig. 5. It was observed that as the flow-rate increased, the response of the system increased until it reached a maximum point, beyond which it remained constant. This result can be explained as follows. The resistance to mass transfer in the membrane permeation process occurs in three steps: first the migration of VOCs to the membrane surface through a boundary layer, second the diffusion of VOCs through the membrane and third the diffusion into the inert gas on the other side of the membrane. At low flow-rates, the diffusion through the boundary layer may be the rate-limiting step. However, when the flow-rate was increased, more turbulence was introduced, destroying or reducing the boundary layer and increasing the total flux through the membrane. Consequently, the system response increased. However, when the flow-rate was increased beyond a certain point, the response of the system did not increase any further because the rate-controlling step was the diffusion through the membrane.

In Fig. 6, extraction efficiency as a function of flow-rate is presented. It can be seen that the extraction efficiency can be high. At low flow-rates, using only a 10-cm long membrane, more than 80% of the VOCs could be extracted. From Fig. 6, it was also seen that when the flow-rate was increased the extraction efficiency decreased, although the system response increased (Fig. 5). A higher flow-rate brought in a larger amount of the analyte into the membrane module, resulting in an increased mass flow through the membrane. However, high flow-rates also resulted in shorter residence times, leaving less time for permeation. Hence, beyond a certain flow-rate, there was no net improvement in the system response.

3.4. Effect of temperature of membrane module

The effect of the temperature of the membrane module on the system response is shown in Fig. 7. It was observed that at first the responses increased with increase in temperature. Above ca. 70°C, the responses decreased with increase in temperature. This result is consistent with a mechanism in which the decrease in permeability of organic molecules that occurs is due to their reduced partitioning into the membrane at high-

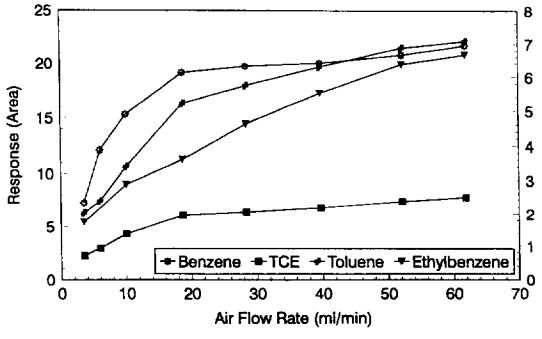

Fig. 5. Effect of air flow-rate on system response.

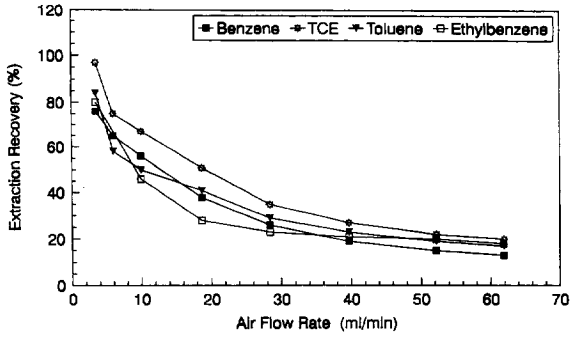

Fig. 6. Membrane extraction efficiency as a function of air flow-rate.

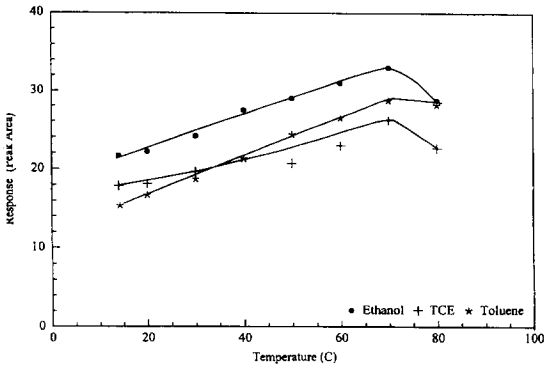

Fig. 7. System response as a function of temperature of the membrane module.

er temperatures. The effect of temperature on the rate of permeation is dependent on the nature of the permeant. The studies conducted by Barrer et al. [19] and Suwandi and Stern [20] showed that the permeability of a silicone membrane for small, non-polar molecules decreases with increasing temperature owing to a decrease in solubility. For larger molecules with larger energies of activation, the permeability increases with increase in temperature. The permeability of analytes through the membrane is a product of diffusivity and solubility coefficient [18]:

$$P = DS$$

where P is the permeability coefficient, D is the diffusivity coefficient and S is the solubility coefficient. The diffusion coefficient increases with increase in temperature and obeys an Arrhenius-type equation [18]:

$$D = D_0 \exp(-E_d/RT)$$

where E_d is the activation energy. Increasing the temperature of the membrane raises the response owing to the increased rate of diffusion. On the other hand, the solubility of VOCs in a silicone membrane decreases with increase in temperature [18]:

$$S = S_0 \exp(-E_s/RT)$$

where E_s is the enthalpy of sorption. At higher temperatures, the decrease in solubility dominates and consequently the response of the system decreases.

3.5. Effect of moisture in membrane permeation

The experiments were performed with humidified samples containing between 0.6 and 47% moisture. The results are presented in Fig. 8. The amount of moisture added is significantly higher than what is normally encountered in ambient air samples, although stock samples may have such a high moisture content. Even at these high moisture contents, the system response did not show any appreciable change.

Permeation is a function of the chemical properties of both the permeant and the membrane. The chemical composition of the membrane substrate plays an important role. The silicone membrane used in this study was hydrophobic and highly permeable to organic compounds, hence the moisture did not effect the permeation of organic molecules. However, if condensation occurs on the membrane surface, the water layer may form a barrier to mass transfer and the system response may decrease. In this experiment, the membrane module was maintained at about 70°C to prevent condensation. The experiment demonstrated that the moisture content of the air sample did not limit the application of the on-line membrane extraction for VOCs monitoring. Hence here membrane extraction acts a water management device by separating water from VOCs. This is very useful for air analysis

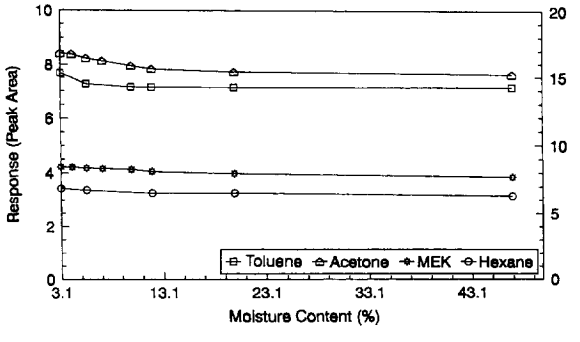

Fig. 8. Effect of moisture content of air on system response.

because moisture has always been a problem in trace VOCs analysis.

3.6. Response time of the analytical system

The response time of the analytical system is an important parameter in continuous monitoring applications. The important factor here is the time taken by a sample molecule to diffuse through the membrane which results in a delay before the system responds to a change in concentration. The response time of the system was studied by injecting a few microliters of the sample vapor into an air stream entering the membrane module. Then the test compound in the strip gas was monitored by pulsing the microtrap every 10 s. There is considerable dead volume in the membrane module and the associated plumbing, which also accounts for a certain time delay. An injection of the same amount of the sample through the module with the membrane removed served as a blank. Hexane, 1,2-dichloroethane (DCE), methanol and methyl ethyl ketone (MEK) were used in this test. The experimental results are listed in the Table 1 and the profiles for hexane and DCE are shown in Fig. 9.

The lag time is defined as the interval between the time the gas comes into contact with the membrane and when it emerges on the other side [21]. Tailoring that definition to this system, considering dissolution and diffusion effects, a differential time lag (DTL) is defined as the difference between T_{max} and T_{blank}. In Table 1, it can be seen that the value of T_{blank} was very similar for all the compounds. The value of DTL depends on the compound and can vary between 0.16 and 1.32 min. The DTL decreased in the order MeOH > MEK > DCE > hexane.

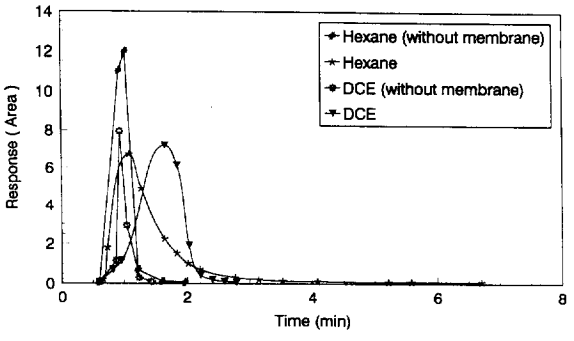

Fig. 9. Response time of the analytical system.

Table 1
Response times of different compounds

Compound	T_{max} [a] (min)	T_{blank} [a] (min)	DTL = $T_{max} - T_{blank}$ (min)
Hexane	1.09	0.93	0.16
DCE	1.66	0.94	0.72
MEK	2.10	0.82	1.28
MeOH	2.12	0.80	1.32

[a] T_{max} = time at which maximum response occurs; T_{blank} = time of maximum response in the blank module.

The calculation of the absolute lag time is complicated because the diffusion process depends on several factors. If the diffusion coefficient of the analyte is constant, the lag time, L, can be calculated using the following simple expression [21]:

$$L = \delta^2/6D_0$$

where D_0 is the diffusion coefficient of the gas and δ is the thickness of the membrane. For a certain compound D_0 depends on concentration, the type of membrane, temperature, cross-linking and chemical nature of the polymer and the structure and polarity of the diffusing molecule. Hence in real situations where the diffusion coefficient cannot be assumed to be constant, calculation of the lag time results in very complex relationships [22].

The size of the molecule is an important factor; smaller molecules tend to diffuse faster than larger molecules. However, for partitioning in the membrane, size of the molecule and polarity are important factors. Larger molecules adsorb more strongly than smaller ones. Non-polar molecules tend to dissolve faster than polar compounds in non-polar silicone membranes. Here, the DTL for the non-polar hexane was smaller than that for DCE which is slightly polar, and much smaller than that for MEK, which is even more polar. Polarity is undoubtedly a major

factor affecting the DTL. On the other hand, although the polarity of MeOH is approximately half that of MEK (dipole moments 1.7 and 3.3 D, respectively [23]) the DTLs were approximately the same. This suggests that the functional group was also a significant factor. The size of the molecule was not a factor here because MEK is larger than MeOH. If size and polarity were the only factors, then the DTL of MEK should have been considerably larger than that of MeOH. Hence it is concluded that the functional group also plays an important role; here the hydroxyl group appears to contribute to a higher DTL than the carbonyl group. Further, the polarities of DCE and MeOH are approximately the same (the dipole moment of DCE is 1.8 D [23]). Nevertheless, the DTL for DCE was approximately half that for MeOH. Here again, the higher DTL is attributed to the hydroxyl group.

4. Conclusion

The study has demonstrated that the on-line membrane extraction–microtrap–GC system can be used to provide continuous, real-time monitoring of VOCs in air emissions for measurements at the ppb level. The system exhibited high sensitivity, good reproducibility and response times of the order of 60–90 s. Optimization of the operating conditions was necessary to obtain good results. Another advantage of this system is its ability to handle samples with a high moisture content.

Acknowledgement

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