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Enhancing the performance of membrane introduction mass spectrometry by organic carrier and liquid chromatographic separation

Shi Ouyang, Yong Hong Chen , Yan Xu

Abstract

A method of membrane introduction mass spectrometry with liquid chromatographic separation (LC/MIMS) for the analysis of volatile organic compounds (VOCs) in water has been developed. The method not only inherited all the advantages of membrane introduction mass spectrometry by flow-injection analysis (FIA/MIMS), but also expanded the application of MIMS to the determination of compounds with identical quantitation ions. Because the quantitation by LC/MIMS is based on two-dimensional identification (retention time (t_r) and mass-to-charge ratio (m/z)), it provides a tangible approach to the analysis of VOCs in complex aqueous samples. In this work, a C_{18} column and a mobile phase (methanol/water) were used for chromatographic separation. A mixture of eighteen VOCs was determined within 28 min. The method has linear dynamic ranges of 3–4 orders of magnitude and sub-ppb-level detection limits. In comparison with the EPA method 524.2 (a purge-and-trap GC/MS method), it requires less analysis time and no sample pretreatment.

Keywords: Membrane introduction mass spectrometry; Liquid chromatography; Flow injection; Volatile organic compound; Environmental analysis

Introduction

Trace amount of volatile organic compounds (VOCs) in aqueous solution, as a group of environmentally hazardous chemicals, is usually preconcentrated using a purge-and-trap procedure and analyzed using GC/MS. EPA method 524.2 [1] is a typical example of this approach, which is routinely used for environmental analysis and provides reliable

results for both qualitative and quantitative analyses. However, the method is relatively time-consuming and labor intensive, particularly when many samples are involved. Therefore, it is not suitable for on-site monitoring. With the fast growing knowledge in the toxicity of chemicals and public awareness of environmental problems, the environmental legislation becomes more strict, and requires an on-site analysis and the proof that the discharged materials meet the allowable limits prior to their release to the environment. Under these circumstances, some complementary methods, such as membrane introduction mass spectrometry (MIMS) [2], solid-phase

microextraction (SPME)/GCMS [3], solid-phase extraction (SPE)/Raman spectroscopy [4], and inertial spray extraction mass spectrometry (ISEMS) [5], emerged. Among them, MIMS has received great attention.

MIMS was first introduced in 1963 [6], but it did not receive much attention until the recent flourishing development of this method in the determination of VOCs in air [7], water [8], and blood [9]. In these applications [6–9], flow injection analysis (FIA) was used in conjunction with MIMS. The most distinct advantages of FIA/MIMS over the GC/MS methods in the analysis of VOCs are its rapidity, simplicity, and a low limit of detection (LOD). For instance, each FIA/MIMS analysis takes only about 10 min; neither sample preconcentration nor derivatization is needed; and the LODs of most methods reported range from parts-per-billion (ppb) to parts-per-trillion (ppt).

However, FIA/MIMS does have limitations in the determination of complex VOCs because identification by this technique basically relies on detecting the most intense m/z peak that is unique to each compound in a mixture. In practice, quite often one compound shares the same quantitation m/z with other compounds and results in a false or miss identification [10]. Although these limitations can be overcome by tandem mass spectrometry, it requires more expensive instrumentation and further method development.

Since chromatographic separation is based on the retention characteristics of compounds, the combined use of LC with MIMS provides a practical solution for the forthmmentioned problems in FIA/MIMS. Though the feasibility of LC/MIMS was tested by Jones and Yang in 1975 [11], this paper is the first report on LC/MIMS for the determination of complex VOCs in aqueous solution. In this study, the effect of mobile phase composition and flow rate on the membrane response, and elution conditions of LC were studied; a mixture of 18 VOCs that have identical quantitation ions were determined by LC/MIMS; and the results were compared with that of FIA/MIMS. It has been demonstrated that LC/MIMS not only inherits all distinct advantages of FIA/MIMS, but also is a more reliable analytical technique for the determination of complex VOCs in aqueous solution.

Experimental

Reagents and solutions

All VOC standards (100 ppm in methanol) were purchased from Chem Service (West Chester, PA). Methanol (99.9+%, PRA grade) and hexane were obtained from Aldrich (Milwaukee, WI). Calibration compound for mass spectrometer, FC-43 (perfluorotributylamine), was obtained from Scientific Instrument Services (Ringoes, NJ). VOC stock solutions at 1 ppm level were prepared by 100-fold dilution of the VOC standards in de-ionized water (Barnstead/Thermolyne NANOpure System, Dubuque, IA). VOC working solutions at various concentration levels were freshly prepared prior to the analysis by serial dilution from the stock solutions with de-ionized water.

Instrumentations

The LC/MIMS system used in this study is shown schematically in Fig. 1. It consisted of an LC gradient pump (Dionex GP40, Dionex Corporation, Sunnyvale, CA), a manual injector (Dionex LC5), a C_{18} column (100 mm \times 3.2 mm, 3 μ m, Bioanalytical Systems, West Lafayette, IN), a homemade membrane probe (similar probes can be obtained from MIMS Technology, Palm Bay, FL), a mass spectrometer (Finnigan TSQ45, Finnigan Mat, San Jose, CA), and a VECTOR/TWO data acquisition unit (Teknivent Corp., St. Louis, MO). The FIA/MIMS system was the LC/MIMS system without a separation column.

In both the FIA/MIMS and LC/MIMS experiments, a 1 ml sample loop was used unless otherwise specified. For each injection, about 4 \times loop volume of

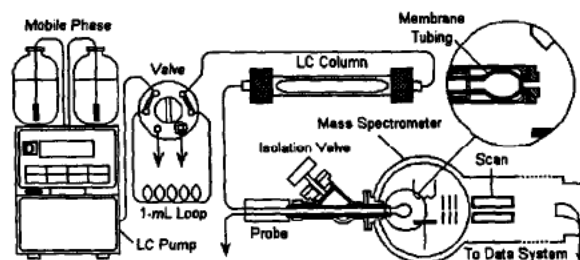


Fig. 1. A schematic diagram of the LC/MIMS system.

sample was delivered by a 10 ml glass syringe (Hamilton, Reno, NV) to avoid any possible dilution.

The membrane probe (Fig. 1) that interfaced the LC with mass spectrometer through a hollow silicone tubing (Konigsberg Instruments, Pasadena, CA) was directly inserted into the ion volume of the mass spectrometer. Prior to use, the silicone tubing that had 2 cm effective length, 0.635 mm i.d. and 1.19 mm o.d. was conditioned by soaking in pure hexane for about 10 min.

In this work, the Finnigan TSQ45 triple-quadrupole mass spectrometer was used as a single-quadrupole mass spectrometer. Nominal integer single ion monitoring (SIM) mode was used, in which the system jumped from one nominal integer m/z to the next over the range 70–150, with a sub-sweep sampling window of 0.4 amu and a scan rate of 5 s per cycle. The ionization mode was electron impact and the ion source temperature was 150°C. Other parameters were 70 eV for ionization energy, 300 μ A for emission current, and 1.5 kV for electron multiplier. Prior to analysis, the instrument was calibrated using FC-43. All mass spectra in this work were taken under these conditions unless otherwise specified.

Results and discussion

Effect of mobile phase composition on dynamic response of MIMS

The dynamic response of FIA/MIMS has been studied theoretically [12]. Generally, introduction of an analyte into an MS through a non-porous membrane is a process known as pervaporation that involves adsorption of the analyte onto a membrane surface, diffusion through its body, and evaporation from the membrane outer surface into the vacuum. The parameters that affect the pervaporation process as well the dynamic response of MIMS include molecular properties of the analyte, membrane material and thickness, diffusion and partition coefficients, sample volume and concentration, membrane cell volume, dispersion in flow conduit, flow rate, and interface mass transfer [12,13]. Once a membrane probe is chosen, the most effective parameters to change the pervaporation rate are

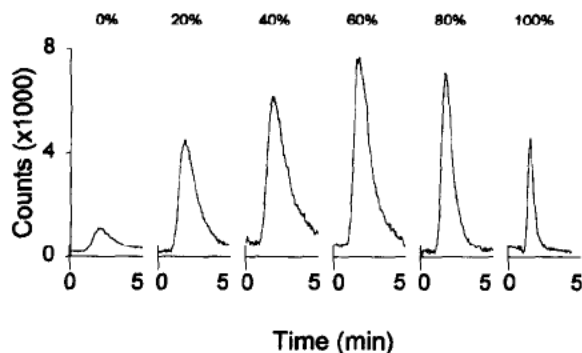


Fig. 2. Effect of percentage of methanol in the mobile phase on the dynamic response of FIA/MIMS. Signals for 1 ppm toluene in water were recorded at $m/z=91$; the sample loop was 25 μ l; and the flow rate was 0.20 ml min^{-1} .

membrane temperature [14] and mobile phase composition, because they have significant influence on the diffusion and partition coefficients of analyte. So far, no report has revealed the effect of organic modifier on the dynamic response of the membrane probe, although some organic solvents have been used as mobile phase and as reagent gas for chemical ionization in MS [15]. Therefore, a series of experiments were conducted to reveal the effect of the percentage of methanol in water on the dynamic response of MIMS.

In these experiments, toluene in water was used as the model analyte for VOCs and the dynamic responses of FIA/MIMS were monitored at $m/z=91$ (Fig. 2). As summarized in Table 1, the peak height of the signal response increased as the percentage of

Table 1
The characteristics of MIMS response

Methanol (%)	Peak height (count)	Peak width ^a (s)	Peak asymmetry ^b
0	934	94	3.7
20	4396	86	3.0
40	6449	85	2.8
60	7249	75	2.7
80	6778	48	2.5
100	4414	26	1.6

^a Peak width measured at the mid-point of the peak height.

^b Peak asymmetry (T) defined as: $T = \frac{B_{0.1}}{A_{0.1}}$, where $A_{0.1}$ and $B_{0.1}$ are the distances measured at 10% of the peak height between the peak front and the peak maximum, and between the peak maximum and the peak end, respectively.

methanol increased, reached the maximum at about 60% methanol, and then gradually declined; the peak width of the response decreased from 94 s to 26 s as the methanol concentration increased from 0 to 100% and the peak asymmetry decreased from 3.7 to 1.6 in the meantime. Obviously, the increase in the methanol concentration not only increased the maximum flux of toluene across the silicone membrane in general, but also reduced the retention of toluene inside the membrane. Such outcome may be explained by the change in the diffusivity and partition coefficient of toluene in the presence of methanol. As compared to water, methanol was more ready to enter the hydrophobic silicone membrane (results are not shown). It enhanced the diffusion of toluene into and through the membrane, thus led to greater toluene flux, narrower peak width, and higher peak symmetry. Moreover, the solubility of toluene in the bulk solution increased with the increase in the methanol content, which altered the partition coefficient of toluene (the ratio of toluene concentration in the bulk solution to that of inside the membrane at equilibrium). As the result of the two opposite effects, a maximum peak height was obtained at about 60% methanol, which represented 7.8-fold increase in the response intensity and more than 20% decrease in the response time in comparison with the results obtained using water as mobile phase (Table 1). This work proved that the modification of the mobile phase is a highly effective way in optimizing the dynamic response of the membrane probe. Although the results displayed in Fig. 2 were based on toluene, they were applicable to all the 18 VOCs studied.

. Effect of flow rate on dynamic response of MIMS

The effect of flow rate on the dynamic response of FIA/MIMS was investigated over the range 0.20–1.00 ml min⁻¹. As shown in Fig. 3, the decrease in the flow rate resulted in an increase in the dynamic response and response time, since the longer residence time of the analyte inside the membrane cell permitted more analyte to pass through the membrane. These findings were consistent with the theoretical prediction [12].

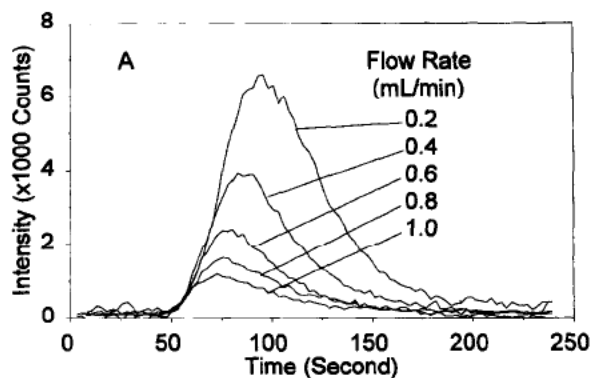


Fig. 3. Effect of flow rate on the dynamic response of FIA/MIMS. 70% methanol in water was used as the mobile phase and the other experimental conditions were the same as in Fig. 2.

. Elution conditions of LC/MIMS

The use of methanol/water as the mobile phase was the key to the success of LC/MIMS, because methanol/water is not only a common eluent in reverse-phase chromatography, but also a better solvent for the MIMS response (see previous discussion on mobile phase). In this work, the elution conditions of LC/MIMS were optimized in terms of separation efficiency, resolution, and dynamic response of the membrane probe. Under optimum conditions, a mixture of 18 VOCs in water was determined by either isocratic elution (70% methanol in water at a flow rate of 0.20 ml min⁻¹ for 42 min) or gradient elution (70% methanol in water at flow rates of 0.60 ml min⁻¹ for 2 min, 0.20 ml min⁻¹ for 16 min, and then changed linearly from 70 to 90% methanol in water during the next 2 min and continued for another 10 min at a flow rate of 0.35 ml min⁻¹). In the case of gradient elution, all the 18 VOCs were determined within 28 min.

. Comparison of FIA/MIMS with LC/MIMS

A mixture containing 18 VOCs (Table 2) was used for a comparison study between FIA/MIMS and LC/MIMS. The reason for selecting these 18 compounds was that many of them have common primary quantitation ions and cannot be identified individually by FIA/MIMS. As shown in Fig. 4, the results of FIA/MIMS and LC/MIMS were recorded in terms of

Table 2
The experimental data of 18 VOCs by LC/MIMS

No.	Compound name	MW	Retention time (min)	Peak width (min)	Quantitation mass ^a			LOD (ppb)
					I	II	III	
					(m/z)			
1	1,3-Dichloropropene	110	7.29	0.75	775	77	110	3
2	1,2-Dibromo-3-chloropropane	234	9.82	0.96	75	77	—	3
3	1,1-Dichloropropene	110	11.48	0.96	75	110	77	2
4	Benzene	78	8.43	0.70	78	77	—	0.5
5	Chloroform	118	6.77	0.77	83	85	—	1
6	Toluene	92	11.48	0.96	91	92	—	0.5
7	<i>p</i> -Xylene	106	15.49	0.92	91	106	—	1
8	Ethylbenzene	106	17.21	1.01	91	106	92	1
9	<i>n</i> -Propylbenzene	120	22.89	1.04	91	120	92	1.5
10	<i>n</i> -Butylbenzene	134	27.58	0.77	91	92	134	1.5
11	Isopropylbenzene	120	20.96	0.98	105	120	77	1
12	1,2,4-Trimethylbenzene	120	24.46	0.78	105	120	77	1.5
13	<i>sec</i> -Butylbenzene	134	26.72	1.01	105	91	77	2
14	Chlorobenzene	112	11.21	0.87	112	77	114	1
15	Carbon tetrachloride	152	11.48	0.96	117	119	121	1
16	Naphthalene	128	16.10	1.03	128	127	129	0.3
17	1,4-Dichlorobenzene	146	16.01	0.94	146	148	111	0.5
18	1,3-Dichlorobenzene	146	18.53	0.94	146	148	111	0.5

^aThe three strongest mass peaks at *m/z* 70–150.

retention time versus relative intensity of total ion current (TIC) and 9 primary selected ion currents (SIC) that had *m/z* values, 75, 78, 83, 91, 105, 112, 117, 128, and 146. In FIA/MIMS (Fig. 4A), the sample of VOCs was directly carried to MIMS without separation. No matter what signal (either TIC or SIC) was measured, only single response peak could be obtained. Quantitation of individual compounds in a mixture by FIA/MIMS is possible only when unique *m/z* ratios are available to those compounds (e.g. peaks 4, 5, 14, 15, and 16 at *m/z* 78, 83, 112, 117, and 128, respectively, in Fig. 4A), otherwise interferences are experienced (e.g. the single peak in Fig. 4A at *m/z*=91 was the total response of five compounds: toluene, *p*-xylene, ethylbenzene, *n*-propylbenzene, and *n*-butylbenzene). In LC/MIMS (Fig. 4B), the sample of VOCs was first separated by a reverse-phase column prior to MIMS. Quantitation in LC/MIMS is based either on the retention time of each compound when several compounds share the identical quantitation ion (e.g. peaks 6, 7, 8, 9, and 10 at *m/z*=91 in Fig. 4B), or on a unique *m/z* if inefficient separation is encountered (e.g. peaks 6, 14, and 15 in Fig. 4B were overlapped at about 11 min on the retention time scale, but they

could be identified by unique *m/z* at 91, 112, and 117). In short, LC/MIMS is a more reliable technique in comparison with FIA/MIMS for the determination of VOCs in complex aqueous samples and the trade-off of the technique is that it has a slightly longer analysis time than that of FIA/MIMS.

It is noteworthy that the peak widths of LC/MIMS were much narrower than those of FIA/MIMS (e.g., peak 5 at *m/z* 83 in Fig. 4) though lower flow rate (that resulted in longer membrane-response time) and longer retention time (that caused band broadening inside the LC column) were experienced in the former case. This is probably attributable to the preconcentration and focusing effect of the C₁₈ column on VOCs from a relatively large size of aqueous sample (1 ml) upon injection, which implied that LC/MIMS may have lower LOD than FIA/MIMS if large size of sample is used.

There were several unassigned minor peaks in most SIC responses of LC/MIMS (Fig. 4B). These peaks were the responses of the secondary or tertiary quantitation ions of the VOCs. Though the intensity of responses are very low in comparison with those of the primary ions, these secondary and tertiary ion peaks are a very useful evidence for a further

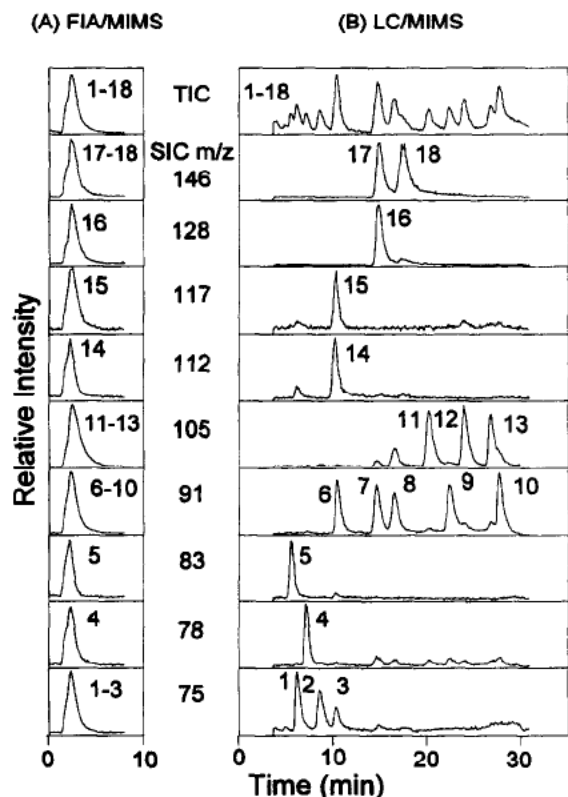


Fig. 4. (A) The responses of FIA/MIMS with 70% methanol in water as the mobile phase at flow rate of 1.00 ml min^{-1} ; (B) the responses of LC/MIMS with gradient elution. The sample loop was 1 ml; the concentration of each VOC was $\sim 20 \text{ ppb}$ in water; and the peak identities were the same as those in Table 2. The narrower peaks were obtained from LC/MIMS than that from FIA/MIMS even as the experimental conditions favored FIA/MIMS in terms of peak width.

confirmation of unknown compounds. In case they overlap with primary ion peaks, their contributions to the total responses are usually negligible, otherwise they can be re-examined using adequate elution conditions.

Analytical merits of LC/MIMS

The analytical performance of LC/MIMS for the determination of 18 VOCs in aqueous solution was evaluated. One example of the 18 VOCs is shown in Fig. 5. Despite the low concentration of naphthalene (1 ppb), a high quality chromatogram was obtained (Fig. 5A) and the mass spectrum of the naphthalene

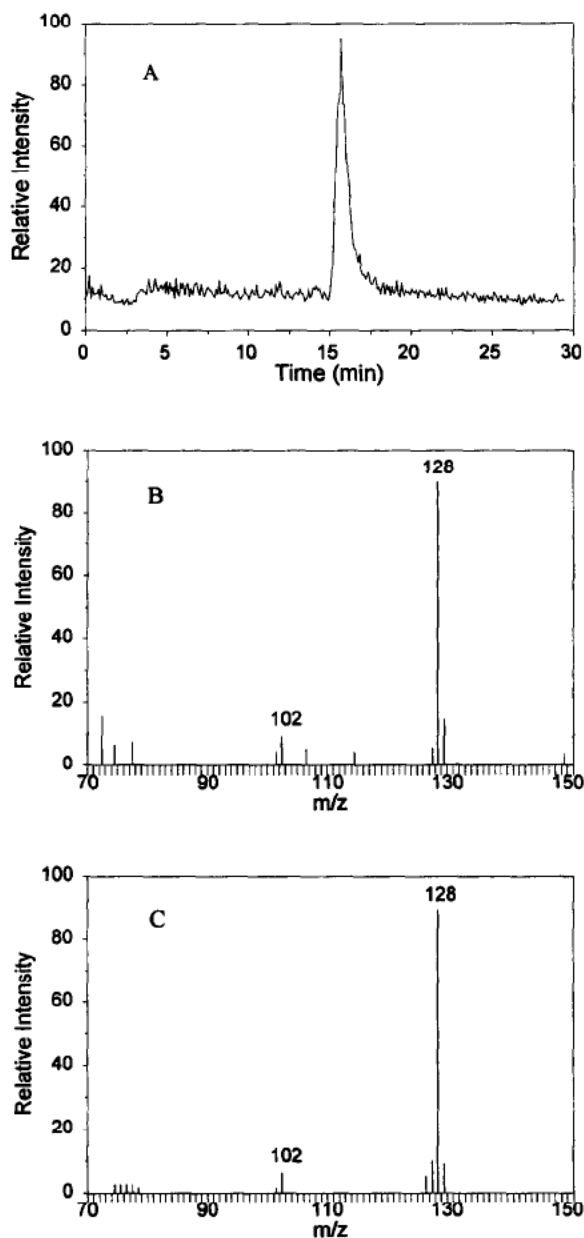


Fig. 5. (A) The response of LC/MIMS for 1 ppb naphthalene ($m/z=128$); (B) the mass spectrum of 1 ppb naphthalene by LC/MIMS; and (C) the mass spectrum of naphthalene from NIST 4.0 mass spectral library. The other experimental conditions were the same as in Fig. 4(B).

solution (Fig. 5B) matched well the standard spectrum in the mass spectral library (Fig. 5C). Other results were organized in Table 2. The retention times

of the 18 VOCs ranged 6.77–27.58 min and the peak widths measured at the mid-point of the peak heights ranged 0.70–1.04 min. The LODs, defined as 3 times S/N from the primary SIC chromatograms, were found in the level range 0.3–3 ppb. The LODs, obtained from LC/MIMS, were quite comparable to those of FIA/MIMS [2], which were related to the solubilities of the VOCs in the silicone membrane as well as the mass sensitivities of the mass spectrometer. Such finding suggested that the limiting factor of the technique is the MIMS detection.

The detection limit of the EPA method 524.2 ranges 0.030–0.33 ppb, about 10 times lower than that of the LC/MIMS method, but the sample size of the EPA method is 25 times larger. On the other hand, further improvement in the detection limit of LC/MIMS is possible because a lower detection limit of MIMS at parts-per-quadrillion level has been reported [16] and there is no sign showing that addition of LC separation will decrease the sensitivity of MIMS method.

In LC/MIMS, calibration curves can be constructed using analyte concentrations versus either peak areas or peak heights of the responses. The linear dynamic ranges of the 18 VOCs found were 3–4 orders of magnitude from the LODs, which covered the routine concentration range for environmental analysis, and the standard deviations of the measurements over the linear dynamic ranges were <6%. Fig.

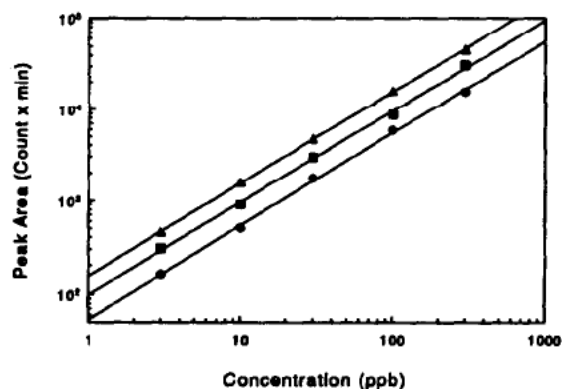


Fig. 6. The calibration curves for three VOCs. (▲) naphthalene, peak area (PA)=153.4 C (concentration in ppb)+150.8; (●) 1,3-dichlorobenzene; PA=51.5 C+166.7; and (■) toluene, PA=102.3 C–353.8. The experimental conditions were the same as in Fig. 4(B). Each datum point was the average reading of three measurements, and r for all these curves ≥ 0.999 .

6 shows the calibration plots for toluene, naphthalene and 1, 3-dichlorobenzene (peaks 6, 16 and 18 in Fig. 4B). Excellent linearities and sensitivities were obtained from the plots. These findings were also in good agreement with those of FIA/MIMS [10].

Conclusions

In conclusion, this study has demonstrated that the combined use of LC with MIMS for the determination of VOCs is practically feasible with the use of methanol-based mobile phase. The dynamic response of silicone membrane can be dramatically improved by the addition of organic solvent in aqueous mobile phase. LC/MIMS is a much more reliable analytical technique than FIA/MIMS for the quantitative analysis of complex VOCs, though the analysis time is slightly increased. LC/MIMS has also been known that LC/MIMS performs at least as well as FIA/MIMS (if not better than FIA/MIMS) in terms of LOD, resolution, linearity, sensitivity, and detection precision. It is a rapid, accurate, and inexpensive alternative to the purge-and-trap GC/MS methods. It provides a new approach for screening, mapping, and quantitating VOCs in aqueous solution.

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