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On-line gas chromatography–mass spectrometry for process monitoring using solvent-free sample preparation

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Abstract

The presented on-line GC–MS system is applied to fermentation processes for the monitoring of potentially toxic volatile organic compounds and semi-volatile organic compounds. The system is based on a simple membrane introduction mass spectrometer. The MS system is coupled to a resistively heated metal GC capillary column. The capillary column serves for chromatographic separation as well as for sample transfer between sampling point and MS system. Solvent-less sampling is performed using a thermal membrane desorption application. Complete sampling and analysis cycles are carried out within 5–10 min. Data is processed on-line and can be used for process control. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Volatile organic compounds; Toluene; Phenol; Cresol; Indole; Naphthalene; Process monitoring; Sample preparation; Thermal membrane desorption

1. Introduction

Process analytical chemistry has different aims. One aim is to observe chemical or biological processes, to record the quality of process streams or to monitor toxic or harmful compounds. Another aim is the on-line monitoring as a base for process control. The latter aim makes high demands on the measurement rate. In both cases the analytical equipment should exhibit sufficient selectivity and has to work autonomically and reliably.

Mass spectrometry and especially membrane introduction mass spectrometry (MI-MS) has been successfully applied to process control [1–4]. Samples are either analyzed directly or after undergoing a fast and simple solvent-free preparation routine.

The main advantages of direct MI-MS are its high sensitivity for volatile and semi-volatile organic compounds (SOCs), which is in the low ppb range [1,5], its mass-selective signals, which allows to identify unknown substances [4] and its short response times of between 10 and 60 s [5] for volatile organic compounds (VOCs). The 'trap-and-release' technique lowers response times and detection limits of direct MI-MS even for high-boiling compounds like 4-phenylphenol or caffeine [6].

Applying solvent-less sample preparation offers the possibility for a chromatographic separation, which provides additional structural information for the analysis of complex sample mixtures.

The use of a PDMS membrane for enrichment and subsequent thermal desorption for the detection of lindane in water and caffeine in beverages was described very early [7]. The detection limits reported are in the low ppb range and low ppm range, respectively.

A widely accepted and very well-described solvent-free sample preparation is the solid-phase microextraction (SPME). SPME with different polymer fibres has been applied to VOCs in water [8] and in

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air [9], as well as to polar compounds [10]. Highly polar and basic diamines have been sampled with a SPME-electrodeposition device [11]. A novel application of SPME is the enrichment of VOCs for UV spectroscopy [12].

Another emerging sample preparation technique for VOCs from water is the membrane extraction with a sorbent interface (MESI) [13]. A very similar system for the extraction of VOCs from air uses, instead of a single silicone hollow fibre (MESI), a membrane module with 20 parallel silicone hollow fibre membranes [14].

The sample preparation technique underlying this work is the thermal membrane desorption application (TMDA). TMDA can be understood as a combination of MESI and SPME. It is an efficient way to hyphenate sample preparation to GC–MS systems because it enables the on-line detection of gaseous compounds and the periodical and quantitative detection of SOCs and VOCs in cycles of a few minutes. In TMDA a polymeric hollow fibre membrane for enrichment is contacted with the aqueous sample. Analytes migrate according to their polymer affinity from the sample into the membrane material. Subsequent to this sorption phase the sample is removed from the membrane. Next the analytes are desorbed by a thermal pulse and carried by a gas stream inside the hollow fibre onto the front of the chromatographic column of the analytical system. The thermal desorption is enhanced by the temperature dependence of solubility and mobility inside the membrane material (Fig. 1).

TMDA has been applied for monitoring the effluent from an industrial waste water plant [15] and for detecting dissolved gases and solutes in fermentation broth [16]. The applied systems showed no or only negligible memory effects, the detection limit for several organic compounds is in the low ppb range [17].

In order to raise the measurement cycle rate, sample preparation as well as chromatographic separation have to be accelerated. A very effective way to perform fast GC runs is by resistive heating of metal capillary columns. GC heating programs with a temperature slope of 9°C/s for crude oil have been reported [18]. A gas sample from an industrial production process containing 33 hydrocarbons from benzene to pyrene has been separated within 10 min with a comparable set up [2]. The separation of a 12-component hydrocarbon mixture from dichloromethane to pyrene has been carried out within 90 s with an extremely small infrared heated GC [19].

The aim of this work has been to set up a reliable on-line monitoring system for gases and semi-vola-

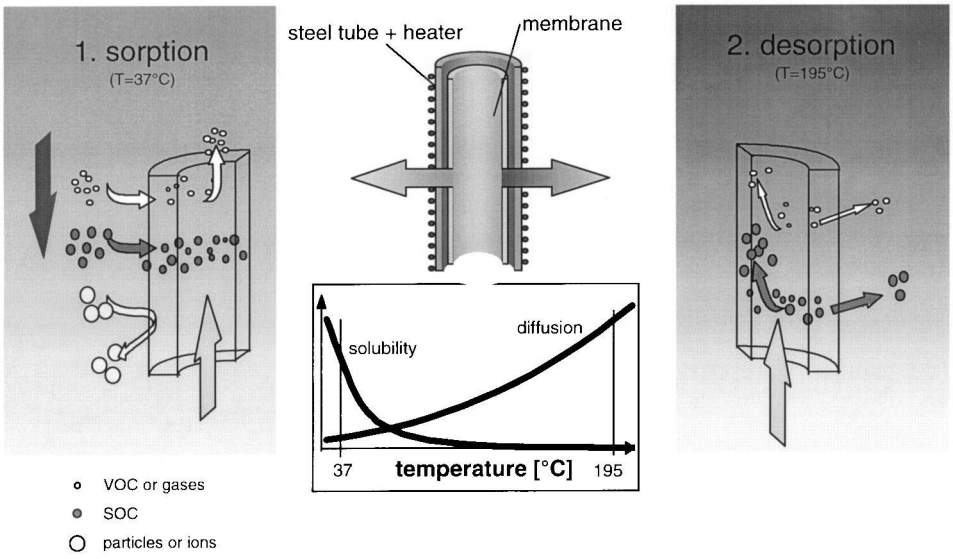

Fig. 1. Sampling with TMDA.

tile compounds for a novel biogas tower reactor [20]. As processes inside this anaerobic reactor are quite slow, a rate of one analysis in 15 min is sufficient.

TMDA is applied for sample preparation. The sample mixture is separated on a 20-m long metal GC capillary column, mounted into a wire-reinforced PTFE tube. The capillary column is resistively heated and coupled to an MS system with membrane inlet.

2. Experimental

2.1. Detector

An electron ionization (70 eV) quadrupole mass spectrometer (Spectra International, Morgan Hill, CA, USA) was used for this work with range 1–200 u and a scanning rate of approximately 70 u/s. The scan width was set to 90–140 u. The secondary electron multiplier was set to 1000 V. The MS system was equipped with a laboratory-made membrane inlet as described in Ref. [16].

2.2. Chromatographic conditions

A metal GC capillary column (Restek MXT-5) with a 3-μm DB-5 stationary phase and an I.D. of 530 μm was used. The 20-m long capillary column served as separation column and transfer line between sampling point and MS system. The set-up of the column is described in Ref. [16].

The injection was performed within 60 s by thermal desorption of the sampling membrane at 195°C.

Temperature programs were applied with a computer-controlled d.c. power supply (Xantrex Technology, Burnaby, Canada). The standard temperature program started after injection at ambient temperature with a slope of 2°C/s up to 200°C. The GC run stopped after 3 min.

The carrier gas was nitrogen of 99.999% purity. The flow-rate varied due to changing gas viscosity between 24 ml/min during injection and 10 ml/min at the end of the GC run.

2.3. Membrane probe

The membrane probe (Fig. 2) is made of a 10-cm long stainless steel tube with an inner diameter of 2 mm. This tube carries a 15-cm long silicone (PDMS-poly(dimethyl siloxane)) sampling membrane (Reichelt Chemietechnik, Heidelberg, Germany): 700 μm I.D. and 200 μm wall thickness.

A coaxial heater (Philips, Hamburg, Germany) is mounted on the tube with silver solder. The membrane temperature is raised by the coaxial heater within 20 s from ambient temperature to 195°C.

In order to optimize sampling different membranes were tested. Polymer type and dimension of the six tested membranes are given in Table 1. The membrane tests were performed with the above-described membrane probe coupled to the mobile GC–MS MEM (Bruker-Franzen, Bremen, Germany) [21]. The chromatographic separation was performed with a 5-m DB1 wide-bore capillary column with a 5-μm stationary phase. Air was used as carrier gas.

2.4. Sampling system

The sampling set-up is outlined in Fig. 3. Analytes are extracted either from a sample off the bioreactor

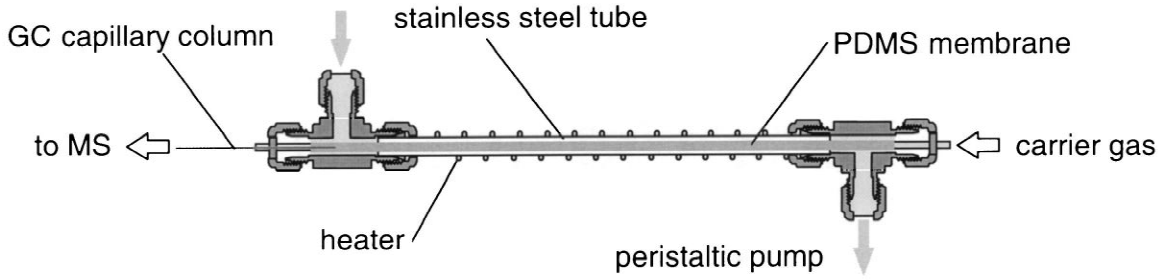

Fig. 2. Membrane probe.

Table 1
Membranes under study for TMDA

Material	Diameter (mm)		Supplier	Remarks
	inner	outer		
PDMS (1)	1.0	1.4	Reichelt Chemietechnik, Heidelberg, Germany	33% (w/w) filler
PDMS (2)	0.3	0.7	Vetter, Ammerbuch, Germany	No filler
PDMS (3)	0.3	0.5	Vetter, Ammerbuch, Germany	No filler
PEBA	2.0	2.4	GKSS, Geesthacht, Germany	
Nafion	1.0	1.27	Ansyco, Karlsruhe, Germany	
PAN	1.0	1.3	Hoechst, Wiesbaden, Germany	Cut off: M_r 30 000

PEBA, poly(ether block amide); PAN, poly(acryl nitrile).

or from an aqueous calibration solution. The liquid is sucked by a peristaltic pump through the small gap between membrane and stainless steel tube. The liquid flow-rate is 20 ml/min. Solutes migrate according to their water phobicity into the membrane material. VOCs partially permeate the membrane, SOCs mainly dissolve in the membrane material. Particles and ions do not interact with the polymer membrane. After sampling the membrane is flushed with tap water followed by removing any liquid with nitrogen. Subsequently thermal desorption injection starts. Simultaneous to the subsequent GC run, a backflush stream of carrier gas through the heated membrane eliminates memory effects.

2.5. Graphic user interface and electronics

The above-described sampling routine is com-

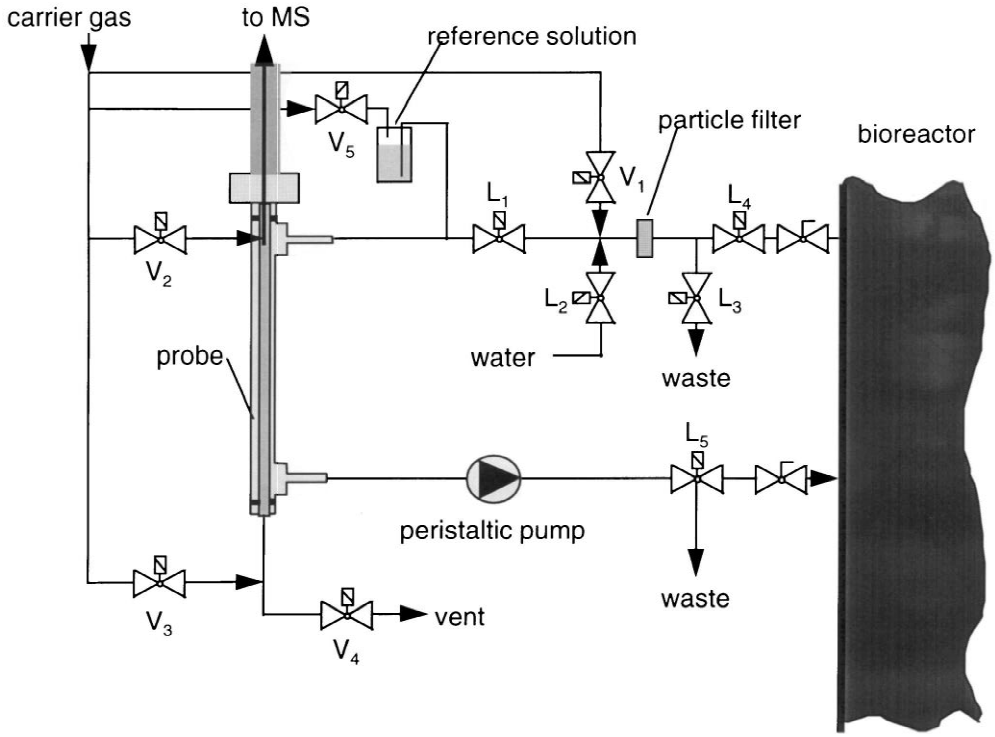

Fig. 3. Sampling set-up.

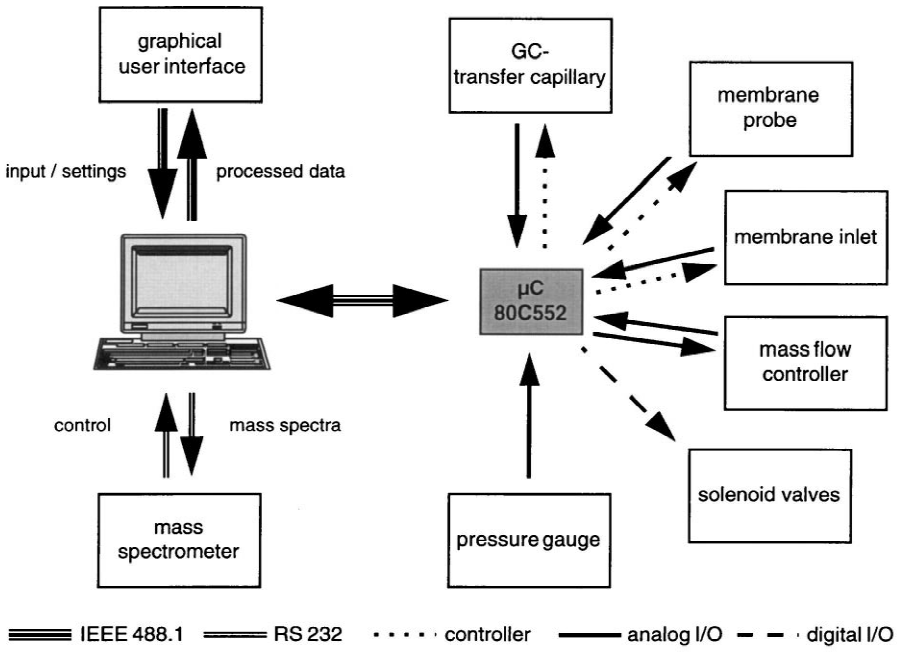

Fig. 4. Organization of sampling, data acquisition and processing. µC, microcontroller.

pletely automated. The hierarchy of data flow is outlined in Fig. 4. The user controls the process with the help of a graphical user interface (GUI), which runs on a personal computer. Data (temperature, concentrations, chromatograms) and system status (current occupation, warnings) are displayed. Sampling or chromatographic parameters and settings can be altered. The GUI has been programmed in LabVIEW (National Instruments, Austin, TX, USA).

Whereas the personal computer is occupied with data processing and controlling the MS system, the actual sampling process is controlled by a microcontroller. Personal computer and microcontroller communicate via the IEEE 488.1 interface. Parameters altered on the GUI are transmitted to the microcontroller and integrated into the process code.

GC–MS data are processed on-line. Six ion tracks, originating from completely recorded mass spectra, are monitored. The selected ion tracks are characteristic for fermentation broth compounds. Every ion track is evaluated within a time window of about the retention time of the respective compound. The MS signals are converted to concentration values, which can be used for process control. The correct operation of the analytical system, as well as quality control of the concentration calculation, is assured by regular intervals of automatic recalibration with reference solutions.

Table 2
Relative standard deviation for several substances; result of 10 measurements

Substance	Concentration (mg/l)	R.S.D. (%)
Toluene	0.5	9.8
Phenol	150	10.1
Cresol	100	11.5
Indol	10	9.6
Naphtalene	0.5	9.2

3. Measurements

3.1. Repeatability

The relative standard deviation (R.S.D.) was determined by repeating analysis cycles with standard solutions. The system R.S.D. for 10 analysis cycles was found to be about 10%, the results are listed in

Table 2. The carrier gas flow-rate varied between the 10 cycles by about ±10%. As the gas flow-rate has a tremendous impact on signal height (see Section 3.5), lower values for the R.S.D. are obtained after integrating a mass flow controller.

3.2. Membrane materials

Three different PDMS membranes were studied, to determine the impact of polymer volume and wall thickness. PEBA and Nafion membranes were tested, as these polymers showed good solubility characteristics for protic polar substances in preceding solubility experiments, whereas PAN is currently used for the enrichment of polar compounds with SPME [10].

The membranes listed in Table 1 were fitted into the membrane probe displayed in Fig. 2. The probe was coupled to the mobile GC–MS MEM. The analysis cycles were as follows: 2 min sampling with a sample flow of 50 ml/min and 1 min thermodesorption injection. Desorption temperatures varied according to the respective thermal stability of the polymers.

Table 3 shows the results of the membrane test in terms of relative selectivity and in terms of relative enrichment. Selectivity is expressed by referring each compounds signal to the naphthalene signal obtained with the same sampling membrane. Enrichment is expressed by standardizing the signal of each compound to the respective signal obtained with the PDMS (1) membrane.

As can be seen from Table 3, Nafion and PAN show in comparison to PDMS a preference for protic polar substances. The good solubility characteristics of PEBA for acetic and propanoic acid could not be exploited. The decisive drawback of the above three membranes is their low thermal stability. PEBA melts at about 160°C and is destroyed even by slight contact with the heater. Heating the Nafion membrane to more than 120°C changes the polymer's colour from a transparent orange to brown (160°C) and black (180°C). The membrane is plastically deformed at temperatures about 160°C. PAN turns brittle at temperatures higher than 120°C and changes its colour from pale white to a deep orange at temperatures between 140 and 180°C. The mentioned low thermal stability and polymer alteration result in an unacceptable low repeatability and membrane lifetime. The R.S.D. for the repeatability of four experiments with the PAN membrane has been determined to be between 70 and 150%. Due to plastic deformation, experiments with the PEBA membrane at 140°C and with the Nafion membrane

Table 3
Results of membrane test

Membrane	Acetic acid	Propanoic acid	Toluene	Phenol	Indole	Naphthalene	Desorption temperature (°C)
Selectivity							
PDMS (1)[a]	0.70	2.58	23.69	0.34	0.67	1.00	200
PDMS (2)[b]	0.00	0.00	3.47	0.00	1.56	1.00	200
PDMS (3)[b]	0.00	0.00	1.50	0.00	0.74	1.00	200
PEBA[c]	0.00	0.00	46.91	0.00	0.00	1.00	140
Nafion[c]	3.21	3.83	8.15	0.63	0.26	1.00	160
Enrichment							
PAN[c]	7.68	8.30	1.54	1.13	1.01	1.00	125
PDMS (1)[a]	1.00	1.00	1.00	1.00	1.00	1.00	200
PDMS (2)[b]	0.00	0.00	0.01	0.00	0.20	0.08	200
PDMS (3)[b]	0.00	0.00	0.02	0.00	0.37	0.32	200
PEBA[c]	0.00	0.00	0.23	0.00	0.00	0.11	140
Nafion[c]	4.84	1.52	0.34	1.88	0.38	0.99	160
PAN[c]	25.26	7.30	0.18	7.13	2.70	1.94	125

Composition of test solution: acetic acid, 10 g/l; propanoic acid, 10 g/l; toluene, 4.7 mg/l; phenol, 84 mg/l; indole, 43.5 mg/l; [$^2H_8$]naphthalene, 2 mg/l.

[a]Data from average value of four experiments.

[b]Data from average value of three experiments.

[c]Data for PEBA, NAFION and PAN: see comment in Section 3.2.

at 160°C could only be carried out once with each membrane. As a consequence, the data for PEBA and Nafion presented in Table 3 have not been derived from average values.

On the contrary, the high thermal stability of PDMS combined with its good permeability is the decisive advantage of this material. Comparing the three PDMS membranes with each other it turns out that the PDMS (1) type is suited best in respect to detected compounds as well as in respect to enrichment. The ratio of polymer volume between PDMS (3), PDMS (2) and PDMS (1) is 1:2.5:6, the membrane surface ratio is 1:2:8.

It is obvious that the protic polar compounds (acetic and propanoic acid and phenol) have been detected only with PDMS (1). In contrast to PDMS (2) and (3), PDMS (1) contains 33% (w/w) of inorganic filler. As a positive impact of the zeolite silicalite on the selectivity of PDMS membranes has been reported [22,23], it is assumed that the inorganic filler is responsible for the higher affinity of PDMS (1) towards protic polar compounds.

The results for indole and naphthalene can partially be explained by the different ratios of membrane volume and surface, and by the fact that the measurements have not been performed at steady state. The time to reach a steady state in the membrane depends on the solute mobility within the membrane and on membrane thickness [16]. The sampling time of 2 min is too short for indole and naphthalene to reach a steady state in a 200-μm thick membrane (PDMS (1) and (2)) (see Section 3.5).

3.3. Linearity and sensitivity

The proof for linearity is very important for the presented set up, because the recorded MS signals are converted with a simple linear interpolation to concentration values. The basis for this interpolation is recalibration with an aqueous standard solution. Data describing the linear behaviour of TMDA–GC–MS are given in Ref. [16]. Linearity has been checked with the presented set-up for a lower concentration range. Results are given in Table 4.

3.4. Quality of processed data

The quality of the processed data is directly linked to the repeatability of a single measurement.

It is assumed that the errors of a single measurement follow the standard distribution, and that the error for a standard solution is the same as the error for a real sample. The MS signal of a real sample is converted to a concentration value by the following linear relation:

$$C_{rs} = S_{rs} C_c / S_c$$

where C_{rs} is the derived concentration of real sample, S_{rs} the signal of real sample, C_c the concentration of standard solution, and S_c is signal of standard solution.

If one applies the gaussian law of error propagation for a random error the result for the error of the derived concentration value $E(C_{rs})$ is:

$$E(C_{rs})/C_{rs} = 2^{0.5}\text{R.S.D.}(S_c)$$

The R.S.D.(S_c) of different substances have been evaluated in Section 3.1 (Table 2).

3.5. Characteristics of sampling time, injection, GC run and membrane inlet

Sampling time has been altered between 1 and 3 min to determine the impact of this parameter on signal height. Table 5 gives the results normalized on 3-min sampling. Toluene as a typical VOC quickly permeates into the membrane polymer and the signal hardly changes between 2 and 3 min. In contrast, the

Table 4
Linearity of TMDA–GC–MS for several substances

Substance	Conc. range (mg/l)	Corr. coeff.	Detection limit (mg/l)
Toluene	0–1	0.996	0.25
Phenol	0–300	0.936	50.0
Cresol	0–300	0.924	20.0
Indole	0–20	0.998	2.0
Naphthalene	0–1	0.978	0.05

Table 5
Impact of sampling time on signal height

Sampling (min)	Toluene	Phenol	Cresol	Indole	Naphthalene
1	0.66	0.83	0.77	0.68	0.57
2	0.93	0.91	0.91	0.71	0.60
3	1.00	1.00	1.00	1.00	1.00

Table 6
Impact of injection time on signal height

Injection (s)	Toluene	Phenol	Cresol	Indole	Naphthalene
30	0.63	0.32	0.19	0.18	0.28
60	1.18	1.06	0.91	0.72	0.83
90	1.00	1.00	1.00	1.00	1.00

signal of naphthalene noticeably rises with sampling time. Indole takes an intermediate position. Phenol and cresol are more polar substances, which inhibits their absorption by PDMS and explains the lower system sensitivity.

Phenol and cresol show nearly the same dependence on sampling time as toluene. As these com-

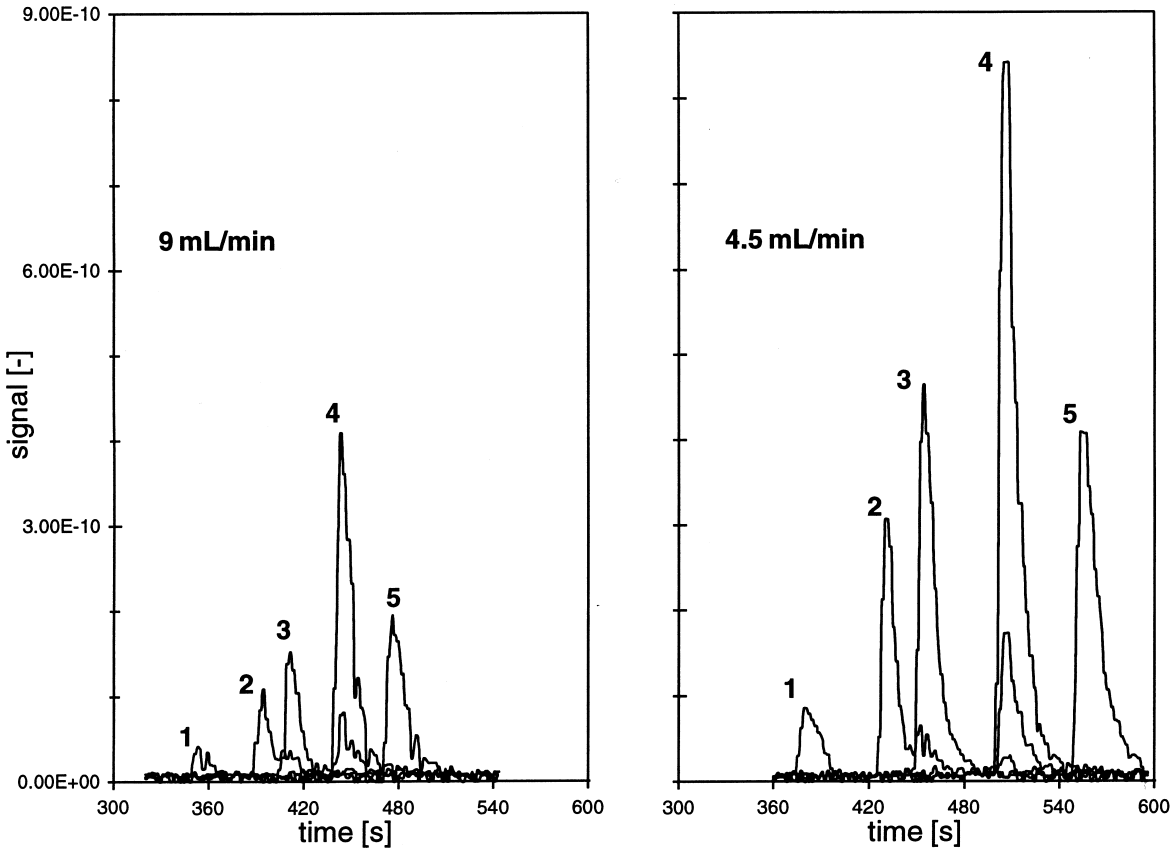

Fig. 5. Fast (left) versus slow (right) GC run; temperature program starts at 270 s. Peaks: 1, toluene (0.5 mg/l); 2, phenol (150 mg/l); 3, cresol (100 mg/l); 4, naphthalene (0.5 mg/l); indole (10 mg/l).

pounds have a comparable molecular radius, it is assumed that the polarity of phenol and cresol has no remarkable impact on their mobility within the membrane polymer. Further experiments have to be performed to confirm this observation.

Injection times have been varied in order to study the characteristics of desorption. Four different types of injection modes have been applied: 30, 60 and 90 s of desorption injection, and 60 s of desorption with injection during the second 30 s of desorption only (30+30 mode).

Between the 30-s desorption injection and the 30+30 mode only a slight advantage for the latter has been observed, whereas a noticeable increase in signal height has been stated between 30 and 60 s of injection. Only indole and naphthalene showed any signal alteration, when injection time rose to 90 s (Table 6). These data correspond with the sampling time data: toluene due to its high volatility desorbs very fast in contrast to naphthalene as a semi-volatile compound. The discrepancy between the 60-s injection and the 30+30 mode suggests that a large part of substance vanishes to the outer surface of the sampling membrane during the 30 s of desorption prior to injection.

The flow-rate of carrier gas during injection and/or GC run noticeably influences signal height. Reducing the injection carrier gas flow from 24 to 15 ml/min cuts signal intensity to about 50%, as well as raising the flow-rate during the GC run from 4.5 to 9 ml/min (Fig. 5). This untypical relation between gas flow-rate and signal height is due to dynamic sorption–desorption processes at the inlet membrane of the MS system. A consequence of this observation is,

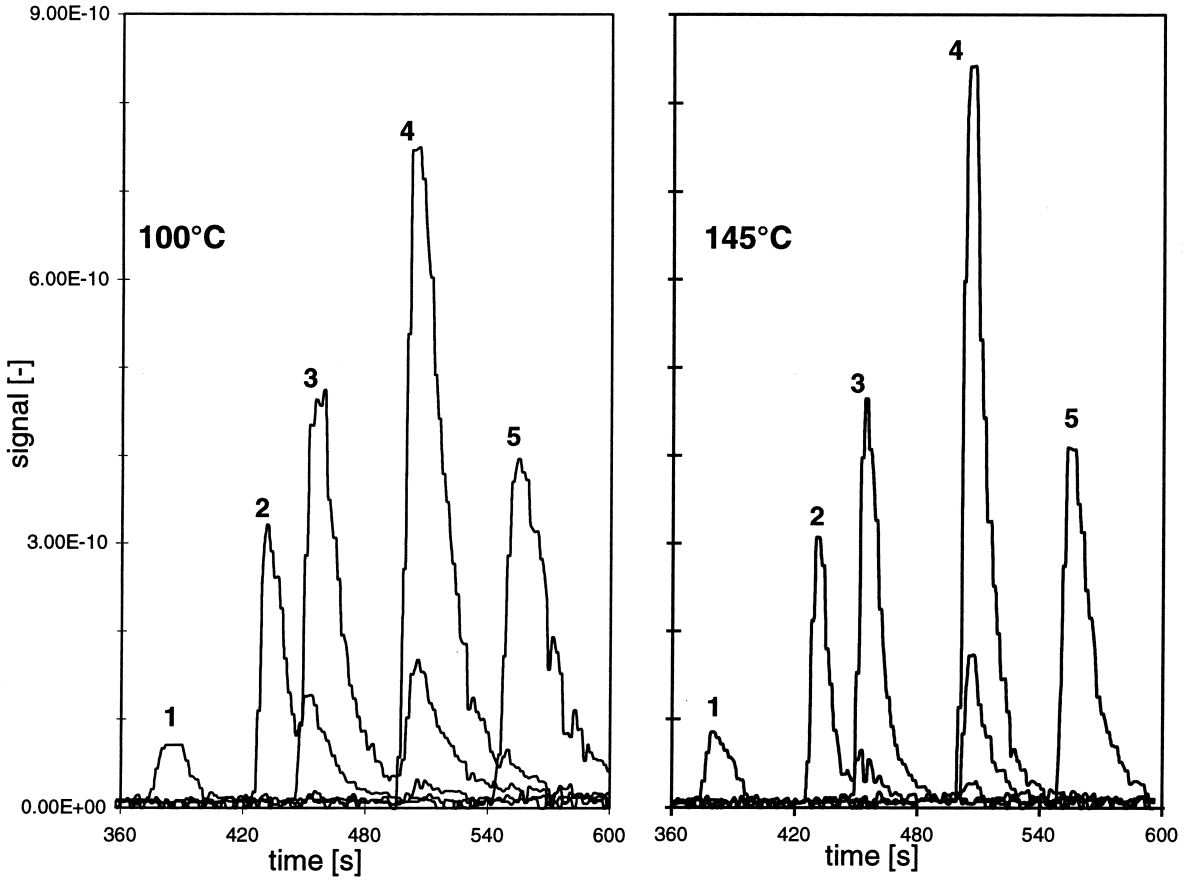

Fig. 6. Peak broadening by inlet membrane; temperature program start at 270 s. Peaks and concentrations as in Fig. 5.

if the analysis cycle time has to be reduced, for instance by speeding up chromatography, that a reduced sensitivity has to be accepted.

The temperature dependence of diffusion and solubility in polymers suggests that the temperature of the MS inlet membrane had a strong impact on the detector signal. Measurements have been performed at 100, 130 and 145°C membrane temperature. An evident signal alteration has not been detected in signal height, but in signal shape (Fig. 6).

4. Conclusion

The TMDA–GC–MS system operates reliably and shows a good reproducibility with an R.S.D. of about 10%. Due to its complete automation it is easy to operate. The analysis cycle time depends on sampling time and GC carrier gas flow-rate. Both parameters have significant impact on the system signal. The applied PDMS sampling membrane is very well suited for aprotic polar and nonpolar compounds. The lack of selectivity for protic polar substances can be partially compensated by filler containing membranes. The positive solubility characteristics of PEBA, Nafion or PAN for low fatty acids could not be exploited by TMDA.

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