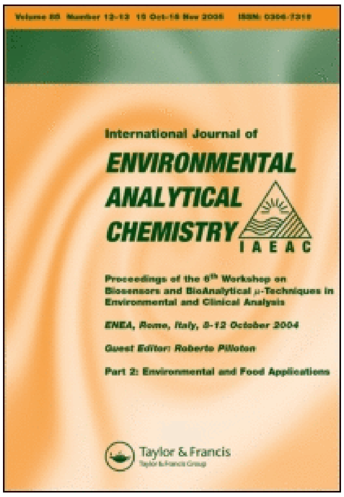

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On-Line Combination of a Silicone-Tubing-Probe Measuring System with HRGC for the Analysis of VOCs from Water Samples

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ON-LINE COMBINATION OF A SILICONE-TUBING-PROBE MEASURING SYSTEM WITH HRGC FOR THE ANALYSIS OF VOCs FROM WATER SAMPLES

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A Silicone-Tubing-Probe measuring system with SnO_2 sensor, based on the permeation of volatile organic compounds from a water sample to the gas phase through a dimethylsilicone membrane, was used for in-situ analysis of VOCs. The SnO_2 sensor was used for the continuous determination of the sum of organic compounds liberated from the water sample. On-line combination of the measuring system with capillary gas chromatography enabled the determination of individual compounds and the study of the analyte permeation processes. The system was tested by using selected aromatic hydrocarbons, oxygenated and chlorinated compounds in water as simulated samples. The compounds were isolated from the water matrix and analyzed in the 10 μg/l — 400 mg/l concentration range. The combined Silicone-Tubing-Probe system can be used for monitoring volatile organic compounds in water samples.

Keywords: Membrane permeation; monitoring system; gas chromatography; VOCs; water

INTRODUCTION

The determination of the contaminants present at low concentrations in water samples is a complex problem that requires the use of preconcentration methods and techniques for the isolation of analytes from the water matrix. The samples are very often incompatible with direct injection into a chromatographic system or the concentration of the analytes is lower than the method detection limit. The techniques used for the isolation and preconcentration of volatile and semivola-

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tile pollutants in water can be divided into the following groups[1–3]: liquid-liquid extraction, solid phase extraction (including membrane extraction) and gas phase extraction (static and dynamic headspace). A number of separation techniques employing membranes for the preparation of samples prior to chromatographic analysis have also been reported[4,5].

Thanks to progress in polymer research, the applicability of membranes in analytical chemistry is increasing. Their use has been extended to the pre-treatment of water and air samples for the chromatographic determination of volatile organic compounds (VOCs). The extraction includes two processes: the isolation of organic pollutants from the sample matrix on the membrane surface and the extraction of pollutants by stripping gas which is subsequently injected into a gas chromatograph. The permeation of VOCs from the water solution through the membrane to the gas or liquid medium is utilized in these processes. Driving forces can be gradients in concentration, pressure, temperature or electrical potential. The quality of the membrane in terms of material and structure determines the possible applications[6]. Membranes of polydimethylsiloxane (PDMS)[7,8], silicone polycarbonate[9,10] and copolymers of styrene[11] and its derivates are most frequently used.

Description of the first type of device for the isolation / concentration of VOCs from a water sample was published in 1984. It was as a passive sampler with a thin membrane of silicone polycarbonate. On immersion into a water sample, the organic compounds permeated through the membrane and were adsorbed onto activated charcoal inside the sampler. The trapped compounds were desorbed from the charcoal by CS_2 and the extract was analyzed by GC[10]. A similar principle was utilized in a technique based on the permeation of the volatile organic pollutants through a semipermeable membrane (silicone polycarbonate) situated in a permeation cell for the analysis of pollutants[11]. This system eliminated the problems associated with the purge and trap technique.

The combination of the isolation of VOCs from the liquid phase by diffusion through a membrane and their detection by sensors represents a progress in monitoring the pollutants in the environment[2]. The Silicone-Tubing-Probe measuring system studied in this paper is also based on analyte permeation from water through the silicone membrane. The stripping gas washing the internal membrane surface is enriched by the analyte and then is led to a SnO_2 sensor. On-line combination of this measuring system with capillary gas chromatography is tested for the direct water analysis without the need for any further treatment of water samples.

EXPERIMENTAL

Benzene, toluene, ethylbenzene p-xylene, butanol and dichloromethane, tetrachloromethane trichloroethylene of the highest available purity (≥ 97%) were used to prepare spiked water samples of individual compounds by dilution in deionized water. The concentration range was approximately 10 µg/l – 400 mg/l depending on the solubility of the analyte in water.

The analyte permeation was studied with the on-line arrangement of Silicone-Tubing-Probe system (STPS) and gas chromatograph (GC) as is shown in Figure 1a.

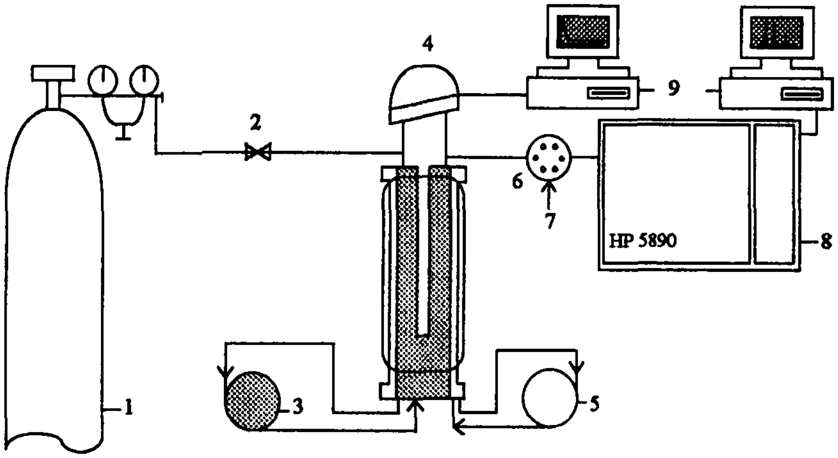

FIGURE 1 a) On-line combination of the Silicone-tubing-probe measuring system with the gas chromatograph. *1*-stripping gas (air) for the Silicone-tubing-probe, *2*-air flow control, *3*-pump for the sample circulation, *4*-Silicone-tubing-probe, *5*-temperature controlled water bath, *6*-six-port valve for gas injection, *7*-carrier gas for GC, *8*-gas chromatograph HP 5890, *9*-personal computer

STPS consisted of a Silicone-Tubing-Probe (Biotechnologie Kempe GmBH, Berlin, Germany), a piston micropump MC 706–300 (Laboratorní přístroje, Prague, Czech Republic) with a constant flow rate of water sample (750 ml/hour), a temperature-controlled water bath MLW (Medingen/Sitz, Freital, Germany) with a platinum resistance Pt-100 thermometer, a PC computer Datas AT for storage and handling of the measured data. The Silicone-Tubing-Probe comprised a stainless steel finger with a gas flow channel, a stainless steel jacketed vessel, a SnO_2 gas sensor TGS#812 (Figaro Eng. Inc., Japan), the electrical connection cap and the stripping gas inlet and outlet (Figure 1b). Compressed air flowing inside the channel with a constant flow rate of 20 ml/min was used as the stripping gas.

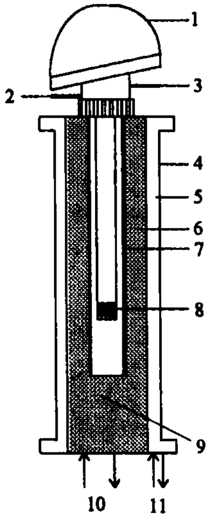

FIGURE 1 b) Scheme of the Silicone-tubing-probe. *1*-electrical connection cap, *2*-stripping gas inlet, *3*-stripping gas outlet, *4*-stainless steel jacketed vessel, *5*-water sample, *6*-thermostatting water, *7*-polydimethylsiloxane membrane, *8*-SnO_2 sensor, *9*-stainless steel finger with channel, *10*-sample inlet and outlet, *11*-inlet and outlet of thermostating water

The probe finger was covered by a tubular polydimethylsiloxane membrane (Reichelt, Heidelberg, Germany). The contact area of the membrane with the liquid sample was approximately 42 cm^2 and the thickness of the membrane was 0.2 mm. The external membrane surface was in contact with the thermostated water sample and the internal surface was washed with the stripping gas. The stripping gas enriched by the volatile analyte passed over the SnO_2 sensor where the adsorption of the analytes on the sensor surface resulted in a decrease in the sensor resistance. This decrease was proportional to the analyte concentration in the gas.

The spiked water sample was continuously supplied into the stainless steel duplicator by a micropump. The temperature of the water sample was controlled to within ± 0.1°C.

The stripping gas was injected by a six-port valve with an external sample-loop (Knauer GmbH, Germany) into the capillary column of an HP 5890 Series II gas chromatograph (Hewlett Packard, Avondale, PA, USA) equipped with a flame ionization detector (FID) in combination with a Sampo computer. The FID-gases were hydrogen (110 kPa) and air (250 kPa), make-up gas was nitrogen (260 kPa) and the detector temperature was 280°C. The carrier gas for the GC was helium (linear velocity 24 $cm.s^{-1}$), and the injected volume of air sample was 650 μl.

The analysis of the spiked water and studies of analytes permeation were carried out using the capillary column CP-Sil 5 CB (25 m × 0.32 mm I.D. × 5 μm film thickness, Chrompack, The Netherlands) under temperature programmed condition.

RESULTS AND DISCUSSION

The Silicone-Tubing-Probe was calibrated by measuring the sensor resistance as a function of concentration for each individual analyte in the water sample. The measured dependence has been fitted by a two-parameter model[12]:

$$c = a_1 R^{a_2}$$

where c is the analyte concentration in water sample, R is the sensor resistance, a_1 and a_2 are parameters.

The determination of the analyte concentrations in a mixture was complicated since the sensor signal for the mixture was not the sum of the signals for individual analytes (Figure 2). The response of the SnO_2 sensor to moisture in the stripping gas is shown also in Figure 2. The problem of compounds separation and quantitation was solved by separation of the gas sample, (i.e. the stripping gas enriched by analytes) by gas chromatography and detection by FID.

Permeation studies by GC

The rate of permeation of benzene, toluene, p-xylene, butanol and trichloroethylene from spiked water samples through the membrane of the on-line STPS/GC system can be envisaged by the dependencies of the analyte peak area on the time of permeation at constant temperature (25°C). A sample of the stripping gas was injected into the gas chromatograph at various times of the analyte permeation. The interval between injections depended on the duration of chromatographic analysis. The peak areas depended strongly on the time of permeation and can be used for an estimation of the time needed to reach the steady state of the analyte permeation. This is illustrated for butanol and benzene in Figure 3. The peak area increases with increasing permeation time and then it remains almost constant after reaching the steady state of permeation. The time to reach the steady state was different for individual analytes: 40 min for butanol, 25 min for trichloroethylene, 30 min for dichloromethane and 20 min for benzene and toluene.

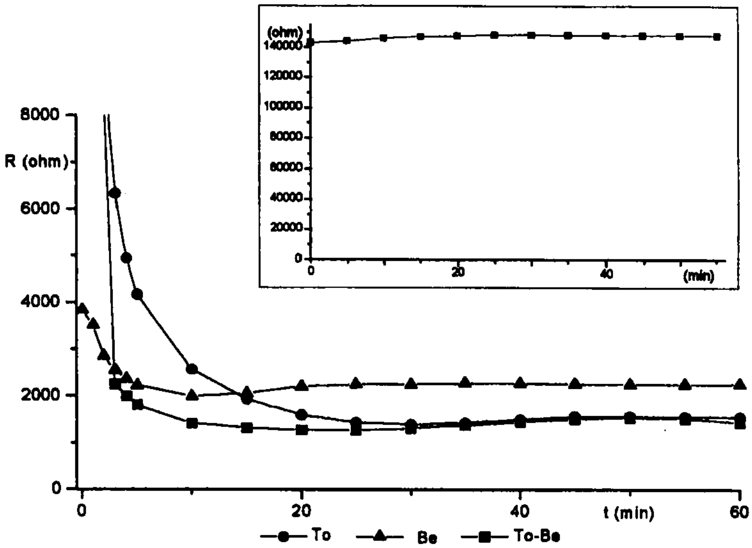

FIGURE 2 Dependence of the sensor resistance on the time of permeation for 100 mg/l benzene (Be), toluene (To) and benzene-toluene mixture; dependence of sensor resistance on the time of permeation for deionized water

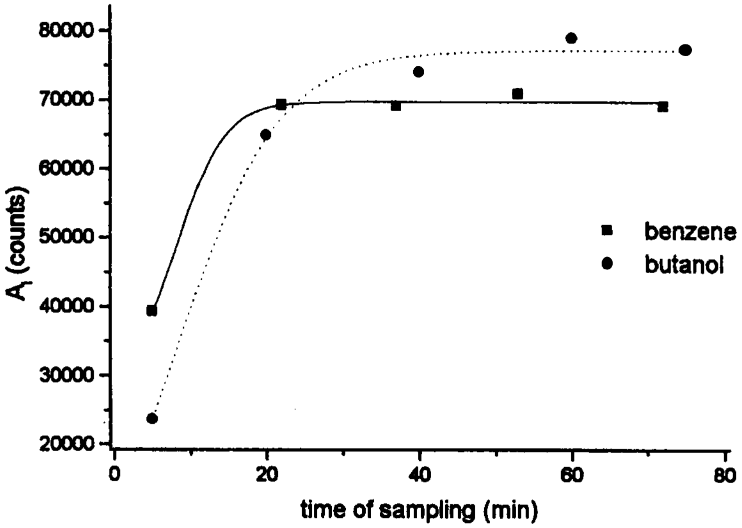

FIGURE 3 Depedence of the peak area on the time of permeation for n-butanol and benzene (cca 40 mg/l of analyte)

Calibration of the combined STPS / GC arrangement

Calibration of the on-line arrangement of STPS / GC was performed by sampling the stripping gas after reaching the steady state of permeation. The dependence of the peak area of an analyte on its concentration in the water matrix was found to be linear for the investigated compounds. The parameters of the calibration curves for benzene, toluene, ethylbenzene, butanol, dichloromethane and trichloroethylene measured at 5 concentration levels in the range 8–80 mg/l with the related correlation coefficients are summarised in Table I. The correlation coefficients are above 0.999 which demonstrates the very good quality of the linear correlation between the peak area and a compound concentration in water.

TABLE I The list of regression parameters

	a [counts]	*b [counts.l/mg]*	*r*
Butanol	1468.7	1752.8	0.9992
Benzene	1924.3	26095.5	0.9999
Toluene	-7058.9	21242.5	0.9993
p-Xylene	-2313.3	19378.5	0.9999
Trichloroethylene	-1830.9	7491.9	0.9992
Dichloromethane	-1982.4	12349.1	0.9995

a – intercept, b – slope of calibration curve, r – correlation coefficient.

Isolation of analytes and subsequent GC analysis

This section of the work was devoted to the efficient chromatographic separation of injected analytes. The gas sample was injected after reaching the steady state of permeation.

The dependence of the sensor resistance on the time of permeation for water – toluene solution at 25°C is shown in Figure 4a (the time of gas sampling is indicated by an arrow). In Figure 4b, the FID chromatogram obtained from the analysis of stripping gas containing toluene injected after 60 minutes of the permeation is shown. All chromatographic measurements were carried out under optimal pressure and optimized temperature program.

A study of the isolation of several compounds from spiked water was performed. The mixture was prepared by dissolving the same volumes of benzene, toluene and trichloroethylene in deionized water (final concentration 440; 430; 730 mg/l). Permeation of the analytes at 25°C was monitored until an approximately constant value of SnO_2 resistance was reached (Figure 5a). After 60 min

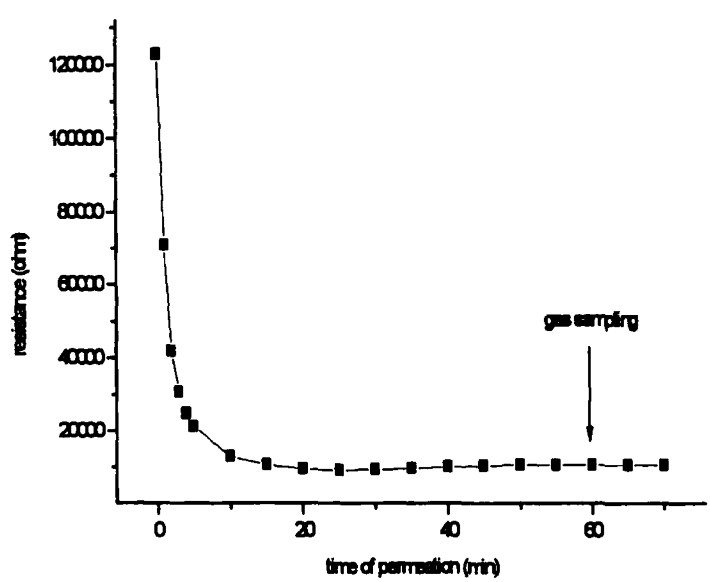

FIGURE 4 a) Dependence of the SnO_2 sensor resistance on the time of permeation for toluene from water (8.5 mg/l) at 25°C with the indication of the time of gas sampling;

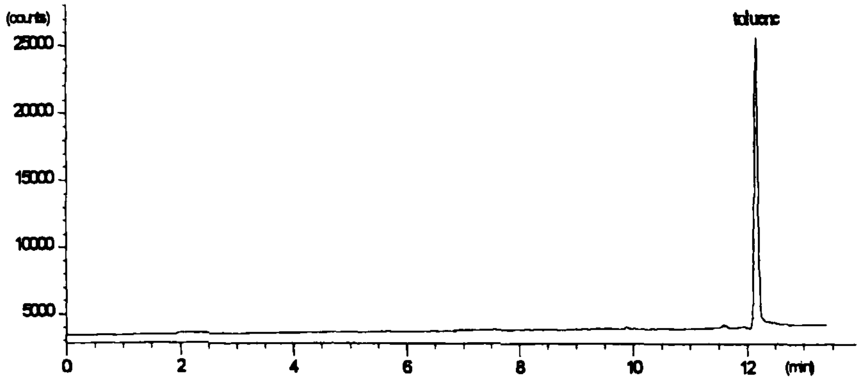

FIGURE 4 b) FID chromatogram of toluene gas sample injected after 60 min of the permeation from the water sample on the CP-Sil 5CB (25 m x. 0.32 mm i.d. x 5 μm film thickness) under temperature programmed conditions: initial temperature 35°C-1 min, temp. gradient 13°C/min, final temperature 180°C, carrier gas helium (u=24 cm/s), temperature of FID 280°C, sampling by six-port valve, injection volume of gas sample 650μl of permeation, the gas sample was injected into the capillary column. The chromatographic separation of a mixture of three compounds after their isolation by permeation from water sample to the gas phase is shown in Figure 5b.

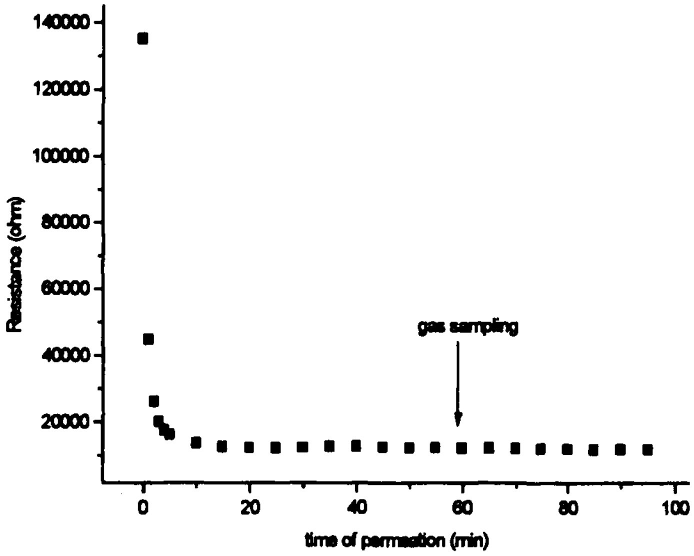

FIGURE 5 a) Dependence of the SnO_2 sensor resistance on time of permeation for benzene, toluene and trichloroethylene from water samples at 25°C (cca 4 mg/l of an analyte);

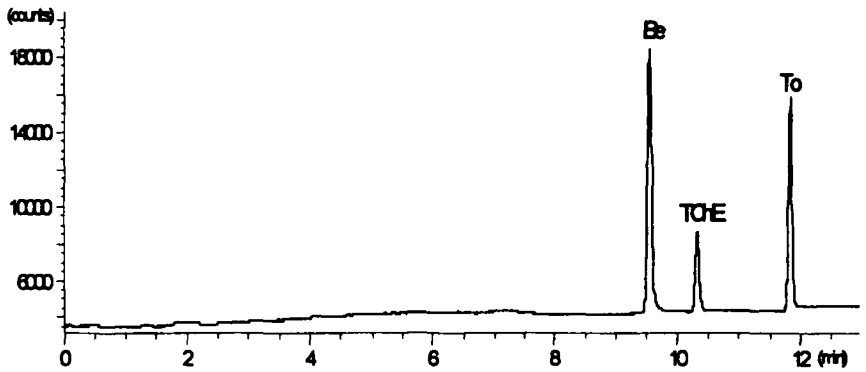

FIGURE 5 b) FID chromatogram of spiked gas sample injected after 60 min of the permeation from the water sample performed on the capillary column CP Sil 5 CB (25 m × 0.32 mm i.d. × 5 μm film thickness) under TPC: initial temperature 27°C – 1 min, temp. grad. 13°C/min, final temperature 180°C – 5 min, carrier gas helium (24 cm/s), temperature of FID 280°C. Peaks: Be – benzene, *TChEt- trichloroethylene, To – toluene*

The chromatographic peak broadenings connected with sampling of the gas phase were reduced by lowering the initial temperature of chromatographic analysis (by CO_2 cryocooling). The chromatographic separation of five selected compounds after their isolation from the spiked water is shown in Figure 6. The concentration levels of the individual components in water were 4 mg/l.

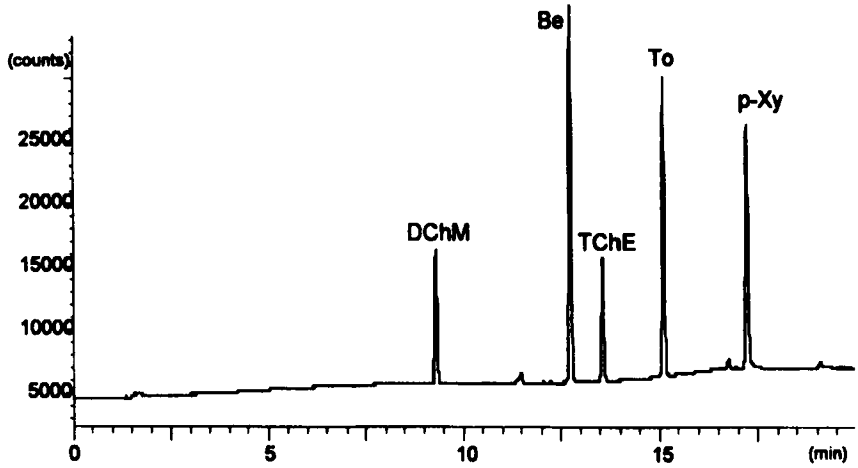

FIGURE 6 FID chromatogram of a simulated gas sample injected at 60 min of the permeation from the water sample. Measurements were performed on the capillary column CP Sil 5 CB (25 m × 0.32 mm i.d. × 5 μm film thickness) under TPC: –20°C – 1 min (cryocooling), grad. 13°C/min, final temp. 180°C – 5 min, carrier gas helium (24 cm/s), temperature of FID 280°C, concentration level 4 ppm. Peaks: DChM – dichloromethane, Be – benzene, TChE - trichloroethylene, To – toluene, p-Xy – p-xylene

TABLE II Determination limits for selected volatile organic pollutants, (n=3)

	determination limit		
Compound	*GC*	*STPS/GC*	
	[pg]	*[pg]*	*[μg/l]*
Benzene	77	262	0.8
Toluene	112	137	2.0
Ethylbenzene	101	162	2.4
p-Xylene	127	141	0.4
Trichloroethylene	231	4874	2.4
Tetrachloromethane	171	2492	274.1
Dichloromethane	265	2649	14.6
Butanol	78.7	2110	544.9

n – number of measurements.

The repeatability of the GC measurements was within 2 to 15 % and that of the sensor resistance within 2 to 9 % depending on the analyte and its concentration. Table II gives a list of determination limits for analytes used in this work (determined as 10-times the standard deviation value of the noise signal divided by the slope of calibration). Benzene, toluene, ethylbenzene, p-xylene, trichloroethylene were detectable at concentrations below 2.4 µg/l and butanol, tetrachloromethane and dichloromethane at higher concentrations.

CONCLUSION

The results show that the Silicone-Tubing-Probe system with SnO_2 sensor is suitable for the direct determination of the concentration of individual compounds in water. The utilization of the combined arrangement of STPS / GC for a complete analysis of organic pollutants in spiked water samples was studied. The selected aromatic hydrocarbons and oxygenated and chlorinated compounds were isolated from the liquid sample by permeation through a thin silicone membrane into the gas phase and subsequently separated by capillary gas chromatography. The rate of analyte permeation was also studied by measuring the dependence of the peak area on the time of permeation. The combined system could be utilized either as a monitoring system or as an alarm system for the detection of VOCs in water samples.

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