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Automated high-capacity sorption probe for extraction of organic compounds in aqueous samples followed by gas chromatographic analysis

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Abstract

An automated high-capacity sorption device for GC analysis of ultra trace components has been developed. The scope of the presented technique was to combine the simplicity of solid-phase microextraction (SPME) with the high extraction efficiency of the stir bar sorptive extraction technology. Sorptive extractions of water samples were performed using polydimethylsiloxane (PDMS) rubber tubing (120 μl) mounted onto a glass rod. The sampling procedure was carried out by a robotic autoinjector. Since the setup is fully automated, unattended and precise time-controlled extraction of samples is possible and makes quantitation with non-equilibrium extractions feasible. The sorption probes are easy to exchange, which facilitates off-line/in-field sampling. The system was evaluated with a test mixture of 44 environmentally hazardous compounds. Detection limits were found to be in the sub-ppt region. The performance of the system was demonstrated with the analysis of polycyclic aromatic hydrocarbons in urban snow.

Keywords: Sorption; Extraction methods; Automation; Water analysis; Environmental analysis; Polynuclear aromatic hydrocarbons

1. Introduction

Gas chromatography remains an indispensable technique for the analysis of trace organic compounds. Therefore, many scientists are still involved in expanding the scope of the technology and/or facilitate the analytical procedures. Most of the fundamental difficulties in analysing natural samples are related to the presence of water and the very low concentration of relevant organic components. Usually, it is therefore necessary to include a preconcentration step. When dealing with aqueous matrices, analyte concentration by sorption or extraction is widely used. For ecological and practical reasons, the use of polymer-based sorbents have replaced many procedures based on solvent extraction.

Solid-phase microextraction (SPME) is probably the best known and most popular technique. This method, which was first described by Arthur and Pawliszyn [1], employs a fibre covered with a film of a suitable stationary phase, mainly polydimethylsiloxane (PDMS), as a sorption medium. The technique is simple and easy to automate and has been used in numerous applications [2]. However, the method has several constrains, which are related to the very small amount of stationary phase employed (<0.7 μl). This limits the extraction capacity, particularly for components with a poor affinity for the stationary phase, thereby impairing the analytical performance for ultra trace components.

Another sorption-based technique for analyte enrichment uses open-tubular traps, coated with a stationary phase (OTT) [3]. The sample is pumped through the trap, while the sample volume passed through the trap is either maintained below the break-through volume of the respective analyte (a procedure known as break-through sampling) [4,5], or where the sample volume is large enough to achieve a state of equilibrium between the two phases [6]. The great advantage of the break-through mode is that it is a quantitative sampling procedure, whereas the yield in the equilibrium mode is dependent of the partition coefficient and is therefore affected by matrix effects. Unfortunately, due to the high mass transport resistance in the liquid phase, OTT

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systems operated in the break-through mode with liquid (water) samples require low flow rates to be efficient [7].

Several years ago, Baltussen et al. [8] proposed a new sorption technique, where a stir bar covered with a PDMS layer is employed (stir bar sorptive extraction, SBSE). The bar is placed in a liquid sample and extraction is accelerated by the rotating movement of the bar during stirring. Once extraction is completed, the stir bar is transferred either to a thermal desorption unit followed by GC [9,10], or extracted with a suitable solvent followed by LC [11,12]. The amount of PDMS depends on the dimensions of the stir bar and thickness of the sorbent layer and is typically 50–250 μl [11,13]. The practical applicability of SBSE has been demonstrated for compounds like polycyclic aromatic hydrocarbons (PAHs) [12,14], polychlorinated biphenyls (PCBs) [15], off-flavor [9], pesticides [13,16], and organotin compounds [17]. These experiments included a wide variety of matrices, such as water, beer, yoghurt, wine, and biological fluids.

However, SBSE has also some drawbacks. Usually, operations like removing the stir bar from the sample, rinsing and drying (optionally extraction, if applied) are performed manually, which is laborious and can introduce errors. Automation of these steps is possible, but this increases the costs and complexity of the hardware involved.

In the present paper, a new procedure for enrichment of ultra trace organic compounds from aqueous samples and subsequent GC analysis is described. The method utilizes the advantages of the large volume of stationary phase in the stir bar (SBSE) combined with the simplicity of SPME. The sampling procedure is fully automated, which allows a time-based non-equilibrium sorption procedure for increased sample throughput. Also, the system is very suitable for analytical applications in on-line process analysis.

2. Experimental

2.1. Instrumentation

The GC instrument was equipped with a split/splitless injector, a mass spectrometric detector (6890 GC and 5973 MSD, Agilent Technologies, USA), a CIS-4 programmed-temperature vaporizer (PTV; Gerstel, Germany) injector and liquid nitrogen cryogenic cooling of the oven (Agilent Technologies part No. G1566A). The chromatographic column was a DB5-MS (30 m × 0.25 mm i.d., film thickness 0.25 μm from Agilent Technologies). The fully automated sampling system was based on a MultiPurposeSampler MPS2 (Gerstel), which was modified in the following way: the regular syringe holder was replaced by a custom made probe holder, shown in Fig. 1A. The new probe holder consisted of a brass rod (12 cm in length and 0.9 cm in outer diameter), in which one hole was drilled from each end (7 and 3 mm diameter, respectively) to fit the silicone rubber probe and the attached glass piston. A gas tight seal between the piston and the top of the brass rod was obtained with a Viton O-ring. A Teflon® ring (see Fig. 1B), ensured a gas tight connection between the entrance of the desorption set-up and the bottom of the brass rod during the desorption stage. A steel capillary tube was brazed onto the upper side of the brass holder. This capillary tube was connected to a needle valve (Swagelok part B-SS1-A). The purpose of this arrangement was to purge the cavity (5 ml/min) between the piston and the brass holder, including the O-ring, in order to avoid a downward migration of possible contaminants. The regular split–splitless injector was used for desorption of the analytes. The top assembly of this injector was modified as shown in Fig. 1B. The regular glass liner was replaced by a Single Gooseneck Silicosleeve liner (Restek, USA), which has a sufficient inner space to accommodate the silicone rubber probe. The regular septum assembly was modified so that a gas tight ball valve (SS-43VS4-1466 Swagelok, USA) could be screwed on top of the assembly. The side entrance of the valve was connected to a restrictor (needle valve, Swagelok B-SS1-A), which allowed a back flush purging (5 ml/min) of the valve. The valve was equipped with pneumatic, double acting actuator (Model 131 DA, Swagelok), to allow automatic switching. Further the GC system was equipped with a regeneration unit (see Fig. 1C). The gas supply and the power to the regeneration unit were controlled as "auxiliary devices" by the gas chromatograph. All steps of the procedure: sorption–desorption–GC-analysis, probe conditioning and switching of the ball valve were controlled by the PAL software (Cycle Composer, CTC Analysis, Switzerland).

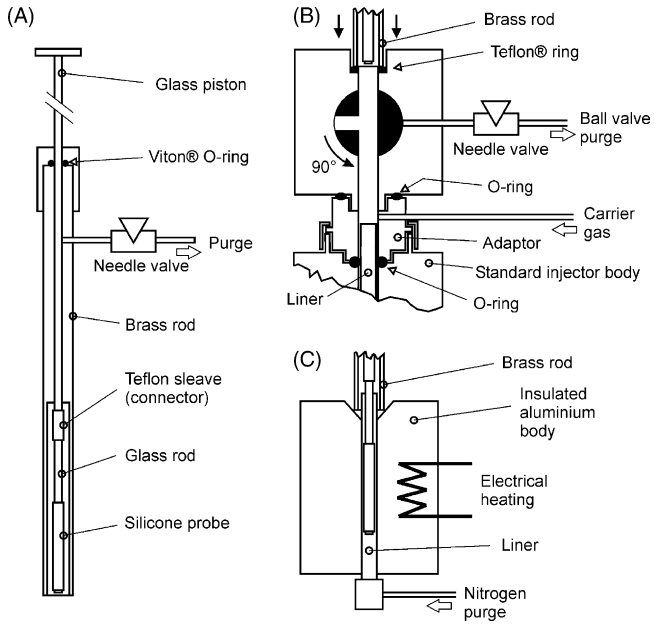

Fig. 1. (A) Probe holder. The purge flow was set to 5 ml/min in all experiments. (B) Top of the desorption unit. Part of the probe holder is also shown as it is pressed against the valve body to achieve a gas tight seal. (C) Regeneration unit with the probe positioned for thermal regeneration.

The sampling probe consisted of a borosilicate glass rod (diameter: 3 mm, length 58 mm), onto which a medical-grade PDMS tube (o.d.: 3 mm, wall thickness: 0.5 mm, Bibby Sterlin, Stone, UK) was mounted. In its final position on the glass rod, the silicone rubber probe had an o.d. of 3.8 mm and a length of 28 mm, resulting in a total volume of 120 μl of PMDS and a mass of 130 μg. The sampling probe was connected to a glass piston (diameter: 3 mm) via a Teflon sleeve of 2.9 mm i.d. and 18 mm in length. This construction enabled a very simple and rapid exchange of the probe, without having to dismantle the entire piston and brass holder. Thus, it is also straightforward to use a set of probes for off-line concentration from different samples, e.g. from remote locations. In this way, the additional flexibility of the stir bar concept is obtained, thus extending the overall versatility of our setup.

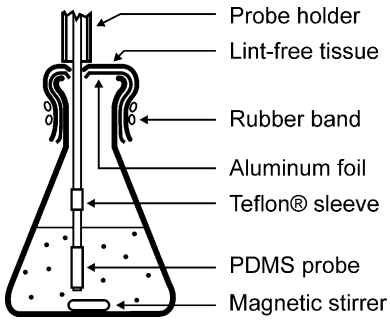

Fig. 2. Schematic drawing of the sample vial used. One layer of aluminum foil followed by three layers of thin lint-free tissue is stretched on top of the vial entrance using a rubber band. When the probe is pulled out from the sample vial, residual water on exposed surfaces of the probe is efficiently removed by the layers of lint-free tissue.

2.2. Chemicals and standards

The calibration mixture consisted of 44 organic compounds [1000 μg of each compound/ml CH_2Cl_2–benzene (3:1)] and was purchased from Supelco (Bellefonte, PA, USA). Deionized water was prepared using a Milli-Q water purification system (Millipore, Bedford, MA, USA). HPLC grade methanol and acetone were purchased from Merck (Darmstadt, Germany). The stock solution of the calibration mixture was diluted with methanol to yield a concentration of 1 ng/μl of each compound. This solution was used to spike water samples to concentrations of 1 ppb/component. For the determination of the detection limit, mixtures with a concentration of 0.01 and 0.1 ng/μl in methanol were also made. All water samples were spiked with hyamine (Sigma-Aldrich, Germany) up to a concentration of 10 μl/l to minimize adsorption of analytes on the glassware [12].

2.3. Sampling and desorption process

All samples were prepared in borosilicate glass 100 ml Erlenmeyer wide neck flasks. Before use, the flasks and glass-coated magnetic stir bars (Cowie Technlology Group, UK) were cleaned as follows: 1 h ultrasonic rinsing in water with detergent, rinsing with copious amounts of Milli-Q water, rinsing three times in acetone, and finally dried at 120 °C under a flow of nitrogen for 1 h. Prior to use, the PDMS probes were conditioned for 6 h at 260 °C in a flow of nitrogen.

The samples were stirred with a glass stir bar at 700 rpm. During the extraction, the flask was covered with a layer of aluminum foil, to ensure separation of the sample from its environment. The foil was covered with lint-free tissue as shown in Fig. 2, the purpose of which was to remove adhered water from the sorbent surface and the glass rod during retraction of the probe from the sample flask prior to desorption. The thermal desorption process was initiated after positioning, lowering and pressing the brass holder against the seal, present in the top of the ball valve (Fig. 1B). The pressure in the inlet was kept low (flow: 1.4 ml/min, pressure: ∼0.5 bar) to prevent rapid expansion of gas into the brass cylinder once the valve was switched. Subsequently, the flow was increased to 4 ml/min at rate of 20 ml/min^2 and was kept at this level for 10–30 min (Section 4). When the pressure was stabilized (after 5 s), the probe was lead inside the inlet liner, kept at 260 °C. During desorption, the GC oven was cooled with liquid nitrogen to −25 °C, which showed to be an adequate cryofocusing temperature for the test compounds used. After desorption, the probe was withdrawn back into the brass cylinder, the ball valve was closed and the probe was inserted in the regeneration unit under flow of 20 ml/min of nitrogen and kept at 260 °C for 10 min, to remove possible remaining traces of analytes and/or contaminants. After this regeneration, a new sampling and analysis cycle was automatically initiated by the PAL and Chemstation software.

2.4. Chromatographic conditions

After completion of the desorption stage, the temperature of the column was programmed from −25 to 35 °C at rate 60 °C/min and then to 300 °C at 10 °C/min. This temperature was maintained for 4 min. For calibration of the GC–MS setup, the PTV injector was used. The temperature of the PTV was started from 35 °C (0.5 min) and programmed up to 300 °C at 100 °C/min. The column temperature was kept at 35 °C for 2 min and then increased at 10 °C/min to 300 °C and maintained for 4 min. Helium was used as carrier gas at a flow rate of 1.4 ml/min.

Detection was carried out using mass spectrometry with electron impact ionization. For examination of sorption profiles, full scan spectra were generated between 33 and 350 μm at 5 scans/s. For determination of the limit of detection and in the applications, the detector was operated in the selected ion monitoring (SIM) mode with 4 cycles/s.

3. Theory

The classical SPME technology is not suitable for ultra trace analysis, particularly when dealing with components which have poor affinity for the stationary phase, due to the very limited amount of stationary phase on the sorption probe [13]. An increased amount of stationary phase, like in the SBSE concept improves this situation. However, another factor to be considered is sampling (sorption) time. This can be crucial in process analysis or in other situations where a large number of repetitive analysis has to be performed. For a given matrix type (e.g. water), the necessary sorption time depends on the type of analytes (their partition coefficients) and concentrations of analytes (lower concentration usually requires longer sorption time and/or larger sample volume to reach the detection limit).

In a case of equilibrium sorptive extraction (ESE), the following equation, describing the extraction efficiency (R), can be used:

$$R = \frac{m_{\mathrm{ESE}}}{m_0} = \frac{(K_{\mathrm{PDMS/W}}/\beta)}{1 + (K_{\mathrm{PDMS/W}}/\beta)} \quad (1)$$

where $K_{\mathrm{PDMS/W}}$ is the partition coefficient of analyte between stationary phase and water (usually substituted by octanol–water partition coefficient $K_{\mathrm{O/W}}$), m_{ESE} the amount of analyte in the stationary phase in equilibrium state, m_0 the amount of analyte originally present in the sample and $\beta = V_{\mathrm{S}}/V_{\mathrm{A}}$ where V_{S} and V_{A} are the volume of the sample and the sorbent, respectively.

One can easily calculate that in our case (where $V_{\mathrm{A}} = 120\,\mu\mathrm{l}$), for a typical sample volume of 10 ml, quantitative extraction ($R > 0.9$) is possible also for compounds with a low K ($\log K_{\mathrm{PDMS/W}}$ around 2–3), and, therefore, quantitative determination is feasible without calibration of the extraction step.

One should take into consideration that the time necessary to achieve the equilibrium increases significantly with the thickness of the sorbent layer as well as the value of the partition coefficient [18]. Therefore, the equilibrium approach should be utilized only in cases when it is absolutely necessary, i.e. when m_{ESE} estimated on the basis of Eq. (1) is close to the detection limit of the detector employed. When large volumes of the stationary phase are employed, like in our high-capacity probe technology, a more attractive approach would be to carry out the extraction under non-equilibrium conditions (see Fig. 3, the "a" and "b" regions). This is an obvious compromise between detectability and analysis (i.e. sorption) time.

The time range from $t = 0$ to a in Fig. 3 represents a special case of non-equilibrium conditions, where the dependence of the amount of analyte extracted versus time is linear. Within this range, the extraction rate is maximal and determined by the flux across the static layer, according to Fick's first law:

$$F = -D_b \frac{\mathrm{d}C_b}{\mathrm{d}r} \quad (2)$$

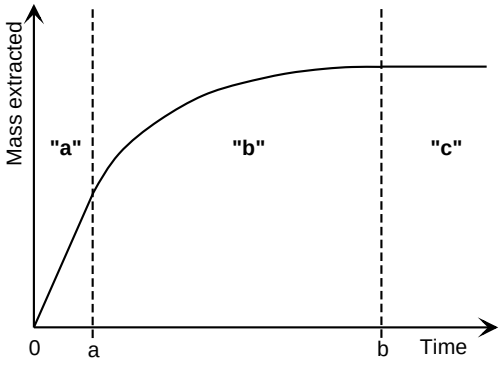

Fig. 3. Dependence of the extracted analyte mass vs. time (a) linear dependence of $m_t = f(t)$; (b) nonlinear dependence of $m_t = f(t)$; (c) equilibrium state.

where F is the flux of the analyte across the boundary layer, D_{b} is the diffusion coefficient of the analyte in a sample matrix, and the term $\mathrm{d}C_{\mathrm{b}}/\mathrm{d}r$ expresses a concentration gradient of the analyte in the boundary layer.

For a given initial flux of analyte (mol s^{-1} m^{-2}), the width of this linear range ($0 < t > a$) depends on the thickness of the sorbent layer and the sample volume. Fig. 4B shows the theoretical dependence of the mass of the extracted analyte as a function of time for two layers of stationary phase, differing in thickness, at constant flux of the analyte through

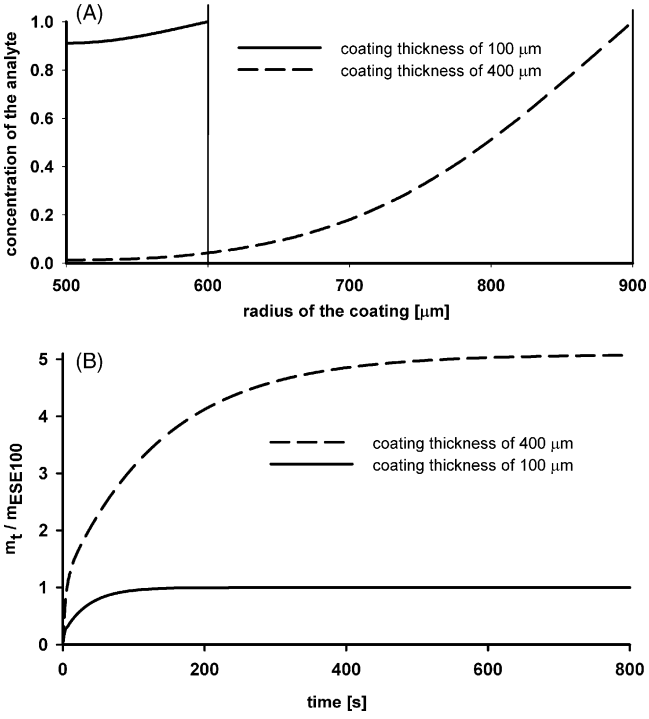

Fig. 4. (A) Calculated concentration profile of the absorbed analyte in two sorbent layers of different thickness. Sorbtion time: 100 s. Diffusion coefficient: 10^{-6} cm^2 s^{-1}. (B) Theoretical extraction profile vs. time for two different coating thicknesses. All parameters are the same as in (A). The value of one on the vertical axis corresponds to the fraction of mass extracted with a sorbent layer of 100 μm in the equilibrium state.

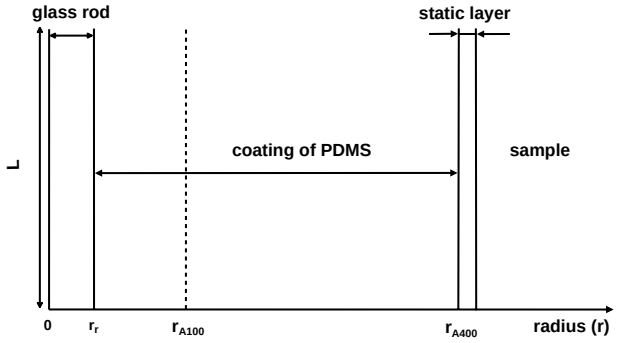

Fig. 5. Schematic model of the sorbent probe where r_r is the radius of the glass rod, and r_{A100} and r_{A400} are the radii of the PDMS layer with thicknesses of 100 and 400 μm, respectively, L is the length of the layer.

a static water layer, ensuring a constant analyte concentration in the external surface of the stationary phase coating. This model may be applied to the sorption process from an infinite volume or from a stream of sample. The calculations were performed using the differential equation of the diffusion for our system (schematically shown in Fig. 5) written in terms of radial coordinates according to [19].

$$\frac{\partial C_A}{\partial r^2} + \frac{1}{r}\frac{\partial C_A}{\partial r} = \frac{1}{D_A}\frac{\partial C_A}{\partial t} \quad (3)$$

where r, radius C_A, concentration of an analyte in the stationary phase; D_A, diffusion coefficient of the analyte in the stationary phase; and t, time.

In order to solve Eq. (3) (to simulate the sorption profile in the coating layer for any given time), taking into account the considerations presented above, the boundary conditions can be formulated as follows:

(a) initial analyte concentration in the stationary phase (coating) is equal to zero:

$$C_A(r, t = 0) = 0 \quad (4)$$

(b) the analyte concentration at the external surface of the coating is and remains constant, being determined by the concentration of the analyte in the sample and by the partition coefficient of the analyte between the sorbent phase coating and the solution:

$$C_A(r = r_A, t) = K_{O/W}C_0 \quad (5)$$

(c) the rod, covered with the sorbent layer is impenetrable for the analyte:

$$\frac{\partial C_A}{\partial t}(r = r_r, t) = 0 \quad (6)$$

Eq. (3) was solved by application of the MATLAB v.6.0 software, employing the finite element method [20]. Fig. 4A shows the relative concentration profile of the analyte, obtained after an extraction time of 100 s, for two sorbent layers of different thickness. As it can be seen, the concentration gradient in the thicker film is steeper. In fact, the flux of the analyte (Eq. (2)) into the thickest sorbent layer is still high while the thinner layer is getting saturated.

Integration of the concentration profiles for different sorption times yielded the graphs, shown in Fig. 4B. These graphs display the mass absorbed over a given period of time for a typical SPME fiber with a film thickness of 100 μm (i.d. = 100 μm, o.d. = 300 μm) and for a fiber of the same i.d., but with coating thickness equal to 400 μm (equal to our probe). In both cases the length of the coating was 1 cm. One can note that the increase in the sorbent coating thickness leads to enhancement of the period when the extraction occurs at a high rate, and consequently, as long as the flux of the analyte into the sorbent exceeds that of the analyte through the static layer, the amount of the analyte absorbed increases linearly in time. An obvious requirement is that the analyte concentration in the sample remains constant (Eq. (2)), which is fulfilled when using a sufficiently large sample volume so that the effect of analyte depletion is insignificant. Thus, the model is very suitable when dealing with the sorption process from a moving stream of the sample, for example a stream of river water or in process analysis.

4. Results and discussion

4.1. Extraction time

The performance of the high capacity probe was tested with a typical environmental pollution mixture of 44 semivolatile organic compounds (SVOCs), listed in Table 1. The compounds represent a broad range of polarity, and, consequently, a broad range of partition coefficients (Table 1). In the first series of experiments, performance of the described probe was examined on the basis of time exposure profiles. Since the purpose of these experiments was to obtain a model, the analyte concentrations used were not extremely low (ca. 1 ppb for each of the analytes). Samples were 100 ml in volume and the extraction time was varied between 5 min and 48 h. In Fig. 6 the obtained extraction recovery versus sorption time for some selected compounds are shown. As can be seen, the equilibrium times are extremely long (>5 h). The time, necessary to obtain complete desorption of the probe was investigated, by desorbing the same probe twice. This time showed to be dependent on the extraction time. For extraction times 5–15 min, 0.5–2 h and >4 h, the times for full desorption were 10, 20 and 30 min, respectively.

The equilibrium extraction efficiency for the compounds under study varied from ca. 10% for bis(2-chloroethyl)ether to above 95% for fluorene. For the seven heaviest PAHs, beginning with chrysene (80%), extraction efficiency at equilibrium started to decrease as the molecular weight increased, and was only 14% for benzo[*ghi*]perylene. This can be due to several reasons, e.g. adsorption of the analytes on the glassware as has been reported by other authors [13].

As mentioned before, full equilibration is not necessary for accurate quantification. The values of the ratio of the ex-

Table 1
Results from the extraction of the 44–component test mixture with the high capacity sorption probe

No.	Compound	CAS	log $K_{O/W}$[a]	Extraction (1 h)			R[d]
				Extraction efficiency (%)	R.S.D. (%)[b]	Yield in (%) of equilibrium recovery[c]	
1	*N*-Nitrodimethyl amine[e]	4164-28-7		–	–	–	–
2	Bis(2-chloroethyl)ether	111-44-4	1.12	5.2	4.7	49.7	0.988
3	1,3-Dichlorobenzene	541-73-1	3.38	28.0	8.0	52.8	0.993
4	1,4-Dichlorobenzene	106-46-7	3.39	27.3	6.7	52.1	0.994
5	1,2-Dichlorobenzene	95-50-1	3.38	28.4	6.7	53.7	0.995
6	Bis(2-chloroisopropyl)ether	108-60-1		14.1	10.8	25.6	0.999
7	*N*-Nitrosodi-*n*-propylamine	621-64-7		8.3	9.0	18.3	0.972
8	Hexachloroethane	67-72-1	3.4	25.3	9.7	63.7	0.994
9	Nitrobenzene	98-95-3	1.88	10.9	6.2	56.2	0.991
10	Isophorone	78-59-1	1.67	5.7	7.3	9.0	0.988
11	Bis(2-chloroethoxy)methane	111-91-1		6.0	8.4	23.2	0.982
12	1,2,4-Trichlorobenzene	120-82-1	3.97	33.1	8.2	55.8	0.995
13	Naphthalene	91-20-3	3.17	21.8	3.2	30.8	0.985
14	Hexachlorobutadiene	87-68-3	4.78	23.6	11.8	61.4	0.988
15	Hexachlorocyclopentadiene	77-47-4		9.4	12.6	63.8	0.953
16	2-Chloronaphthalene	91-58-7		32.9	4.4	39.8	0.998
17	Dimethyl phthalate	131-11-3		6.0	7.4	13.9	0.968
18	2,6-Dinitrotoluene	606-20-2	1.89	14.0	4.9	45.5	0.985
19	Acenaphthylene	208-96-8	3.35	26.1	3.0	31.4	0.990
20	Acenaphthene	83-32-9	4.15	33.3	4.4	38.9	0.998
21	2,4-Dinitrotoluene	121-14-2	1.98	14.4	5.6	34.7	0.983
22	Diethyl phthalate[f]	84-66-2	2.7	–	–	–	–
23	Fluorene	86-73-7	4.02	33.2	3.8	34.7	0.997
24	4-Chlorophenyl phenyl ether	7005-72-3		38.8	6.3	44.8	0.999
25	Azobenzene	103-33-3		28.8	3.7	35.3	0.997
26	4-Bromophenyl phenyl ether	101-55-3		40.6	6.8	45.7	0.999
27	Hexachlorobenzene	118-74-1	6.18	38.2	9.6	52.0	0.999
28	Phenanthrene	85-01-8	4.35	31.7	3.7	33.8	0.995
29	Anthracene	120-12-7	4.35	31.3	3.1	32.9	0.994
30	Carbazole	86-74-8	3.48	23.6	4.3	36.9	0.986
31	Di-*n*-butylphthalate	84-74-2	4.45	24.6	4.8	24.8	0.994
32	Fluoranthene	206-44-0	4.93	30.7	4.2	33.4	0.995
33	Pyrene	129-00-0	4.93	30.2	4.6	33.4	0.995
34	Buthyl benzyl phthalate	85-68-7	4.59	28.4	6.2	36.0	0.992
35	Benzo[*a*]anthracene	56-55-3	5.52	25.1	7.3	31.3	0.993
36	Chrysene	218-01-9	5.52	22.9	7.1	28.7	0.992
37	Bis(2-ethylhexyl)phthalate[f]	117-81-7	7.5	–	–	–	–
38	Di-*n*-octyl phthalate[f]	117-84-0	8.06	–	–	–	–
39	Benzo[*b*]fluoranthene	205-99-2	6.11	13.7	8.0	26.5	0.993
40	Benzo[*k*]fluoranthene	207-08-9	6.11	11.0	7.3	21.3	0.992
41	Benzo[*a*]pyrene	50-32-8	6.11	10.3	6.9	22.3	0.994
42	Indeno[1,2,3-*cd*]pyrene	193-39-5	6.7	4.0	11.0	12.7	0.989
43	Dibenzo[*a*,*h*]anthracene	53-70-3	6.7	3.4	9.1	27.5	0.996
44	Benzo[*ghi*]perylene	191-24-2	6.7	3.2	9.3	23.8	0.991

[a] Water–octanol partition coefficients were taken from reference [21].
[b] Based on five replicate samples.
[c] Values of ratio of the extraction efficiency after 1 h to that at the equilibrium.
[d] Correlation coefficient of the extraction profile in the time interval up to 30 min.
[e] Not included in the study.
[f] No value listed due to high blank levels.

traction efficiency after 1 h to those at the equilibrium are shown in Table 1. These values oscillate between 14 and 64%, with an average of 36% for all compounds. Thus, the detectability will not be compromised to any major extent.

The increased volume and surface area of the sorbent leads to a very high extraction rate at the initial stage. Fig. 7 presents the linear section of the extraction time profile for some of the analytes. The values of the regression coefficients for the linear parts in the time interval up to 30 min for most cases exceed 0.99 (Table 1). It can be assumed that the linear range of the non-equilibrium zone for components with a low partition coefficient will be reduced, since only a small amount of the analyte is needed to saturate the

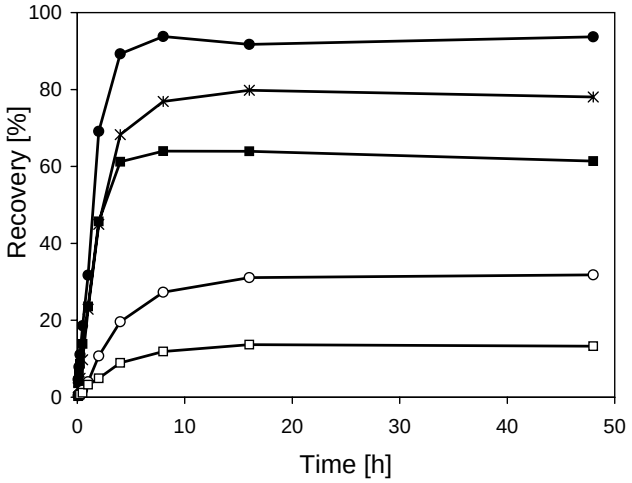

Fig. 6. Sorption profiles obtained for a number of compounds in the mixture. Sample concentration: 1 ppb, (●) phenanthrene, (*) carbazole, (■) chrysene, (○) indeno[1,2,3-cd]pyrene and (□) benzo[*ghi*]perylene.

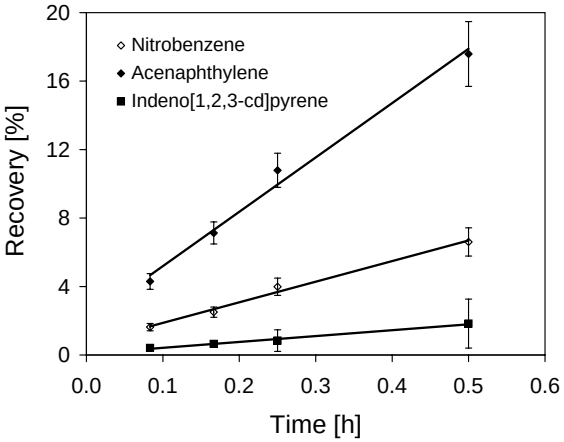

Fig. 7. Sorption profiles obtained at exposure times below 30 min. The standard deviations are shown for each data point as well as the regression curves.

sorbent. Therefore, after a relatively short period of time, the flux of the analyte into the coating becomes smaller then the flux through the static boundary layer. According to the considerations in the theoretical section, conditions allowing linearity of the $m_t = f(t)$ function do not exist anymore after this moment. However, the lower regression coefficients, obtained for some of the compounds do not fully correlate with (low) values of their partition coefficients. More work is needed to investigate this assumption. Nevertheless, after accounting for the specific properties of each analyte, calibration is possible within a reasonable extraction time. Automation of the experimental setup permits full control of both the extraction time and the position of the probe. Such control permitted us to achieve good repeatability of results even for relatively short extraction times (Fig. 7).

4.2. Calibration

Bearing in mind the m_t/m_{ESE} ratio, calibration of the setup was performed using 1 h extraction time. The sample concentrations tested were 0.5, 1, 5, 10, 50 and 100 ng/l. Five repetitive measurements for each concentration were made. In Fig. 8, a chromatogram of the sample, spiked to a level of 5 ng/l, is shown (corresponding to extraction conditions

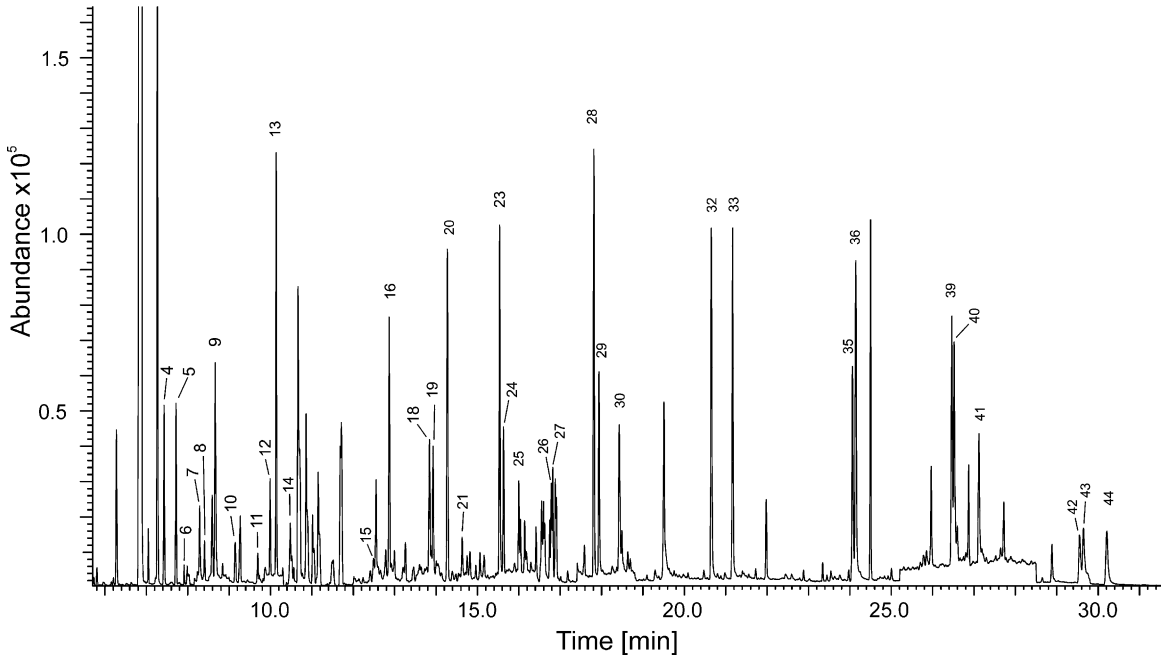

Fig. 8. SIM chromatogram of a test sample containing 5 ng/l of the standard components shown in Table 1. The phthalates were not included in this study due to high background levels.

Table 2
Calibration data for the developed method applied to 17 polycyclic aromatic hydrocarbons. The quantitative data for two replicate analysis of urban snow are also shown

Compound	Target ion		LOD (ng/l)	Run 1 (ng/l)	Run 2 (ng/l)
	[Qualifier ion(s)]	*R*			
Naphtalene	128 (102)	0.9991	–[a]	35.8	34.8
Acenaphthylene	152 (76)	0.9992	0.06	ND	ND
Acenaphthene	153 (152, 154)	0.9987	0.04	7.0	6.9
Fluorene	166 (165)	0.9997	0.07	14.2	13.9
Phenanthrene	178 (152, 176)	0.9977	0.03	153.5	148.2
Anthracene	178 (152, 176)	0.9991	0.06	5.7	2.1
Carbazole	167 (139, 166)	0.9995	0.09	17.1	15.6
Fluoranthene	202 (101, 200)	0.9972	0.03	67.3	65.1
Pyrene	202 (101, 200)	0.9998	0.02	36.7	35.4
Benzo[*a*]anthracene	228 (114, 226)	0.9995	0.02	0.6	0.6
Chrysene	228 (114, 226)	0.9925	0.02	2.9	2.9
Benzo[*b*]fluoranthene	252 (126, 250)	0.9995	0.02	1.2	1.3
Benzo[*k*]fluoranthene	252 (126, 250)	0.9992	0.03	0.3	0.3
Benzo[*a*]pyrene	252 (126, 250)	0.9996	0.04	0.3	0.4
Indeno[1,2,3-*cd*]pyrene	276 (274)	0.9998	0.04	0.4	0.5
Dibenzo[*a*,*h*]anthracene	278 (276)	0.9996	0.06	0.2	0.3
Benzo[*ghi*]perylene	276 (274)	0.9995	0.04	0.3	0.5

[a] Could not be determined due to the presence of a contaminant in the sample at a signal intensity equivalent to approximately 3 ng/l.

from Table 2). Regression coefficients and limits of detection for PAHs are also shown in Table 2. The limits of detection (between 0.02 and 0.09 ng/l) were calculated at a signal-to-noise level of 3:1 and were based on a test sample containing 0.1 ng/l of each compound. It can be expected that the limits of detection will be higher in real-world applications, due to chemical background noise.

The regression coefficients confirm a good linearity in the concentration range under consideration. The excellent performance of the described setup is demonstrated by the

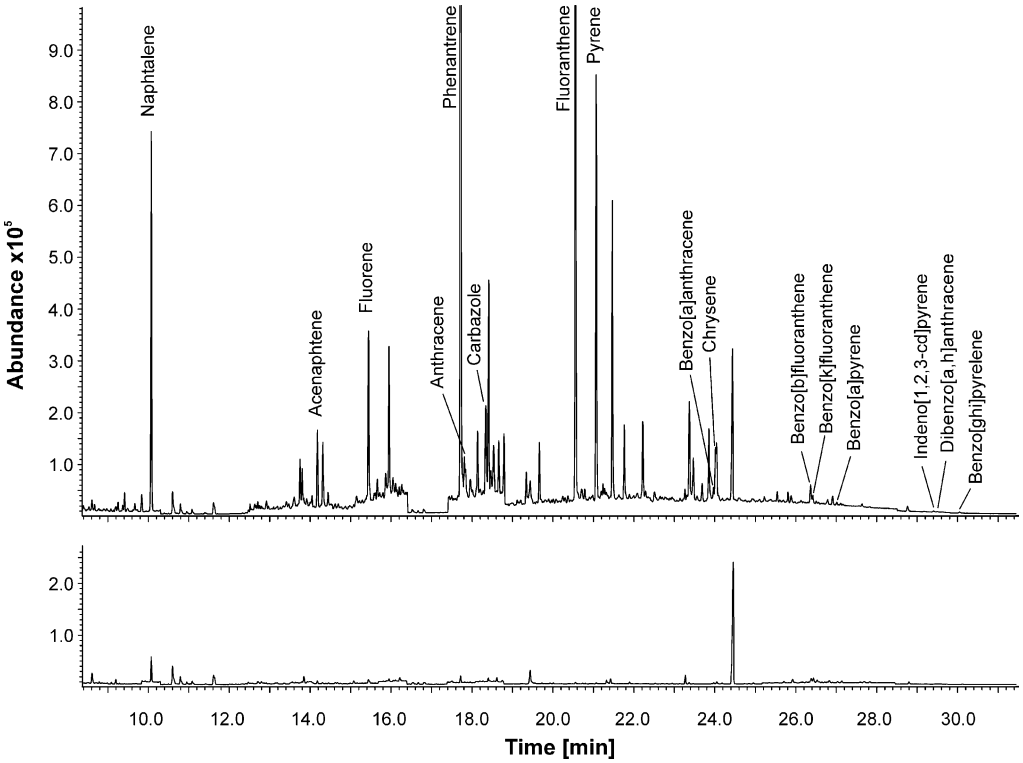

Fig. 9. Application example: 100 ml of urban snow (melted) was extracted by the high capacity sorbent probe for 1 h. This resulting chromatogram corresponds to the data of "run 2" in Table 2.

low limits of detection (sub-ppt level) using a relatively short extraction time.

4.3. Selected application

In the last part of this study, the viability of the described method for real-world sample analysis was tested. The sample was chosen in relation to the composition of the standard mixture, utilized in the evaluation described above. It was assumed that samples of snow from the shoulder of a city street should contain detectable quantities of polycyclic aromatic hydrocarbons. Melted snow (100 ml) was placed in a flask prepared as in the previous experiments. The sample was spiked with hyamine up to concentration of 10 μl/l. The sampling time and chromatographic conditions were the same as in the calibration experiments.

The evaluation included two runs of melted snow samples and three blank runs of Milli-Q water (before, between and after the runs of the snow samples). The blank runs showed no significant cross-contaminations. Typical chromatograms of a sample and a blank run are shown in Fig. 9. The results are summarized in Table 2. The identification of target compounds (listed in Table 2) was made on the basis of qualifier ions, and was further confirmed by retention time data. The comparison of the values, obtained from run 1 and run 2 confirms good repeatability of the method over the whole concentration range. The average amounts of analytes found in the blank chromatograms indicate a minor carry-over, but the contaminations at this low level do not notably affect quantification of the target analytes.

5. Conclusions

A fully automated technique for separation and enrichment of trace organic compounds from aqueous samples is described. The concept combines the advantages of SPME and SBSE technology. The setup is based on a standard GC system and a robot-like auto-injector with minor instrumental modifications. Due to the increased sorbent volume, high efficiency extraction is accomplished. Sorption in a non-equilibrium mode is described and some of the mechanisms involved are discussed in detail. During the initial phase of sorption, the extraction is fast and linearly dependent on the extraction time. This is exploited to reduce the extraction time and facilitates calibration, while sensitivity is largely maintained. The automated and precise control of all chromatographic parameters, including the sorption, desorption, probe regeneration provides a versatile analytical tool for ultra trace analysis, e.g. for environmental monitoring of water. Also, the sampling probe can easily be adapted to sample analytes on-line, either from a by-pass of a mainstream, or by directly exposing the probe to a stream or a bulk volume. Alternatively, sorption probes can be utilized for off-line analyte concentration.

The system was evaluated with a mixture of 44 semivolatile components, relevant to environmental analysis, as well as a sample of melted snow from an urban environment. Detection limits were in the sub-ppt range for polycyclic aromatic hydrocarbons.

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