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Polydimethylsiloxane rod extraction, a novel technique for the determination of organic micropollutants in water samples by thermal desorption–capillary gas chromatography–mass spectrometry

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Abstract

A novel, simple and inexpensive approach to absorptive extraction of organic compounds from environmental samples is presented. It consists of a polydimethylsiloxane rod used as an extraction media, enriched with analytes during shaking, then thermally desorbed and analyzed by GC–MS. Its performance was illustrated and evaluated for the enrichment of sub- to ng/l of selected chlorinated compounds (chlorobenzenes and polychlorinated biphenyls) in water samples. The new approach was compared to the stir bar sorptive extraction performance. A natural ground water sample from Bitterfeld, Germany, was also extracted using both methods, showing good agreement. The proposed approach presented good linearity, high sensitivity, good blank levels and recoveries comparable to stir bars, together with advantages such as simplicity, lower cost and higher feasibility.
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Keywords: Stir bar sorptive extraction; Thermal desorption; Polydimethylsiloxane rod extraction; Extraction methods; Water analysis; Environmental analysis; Chlorobenzenes; Polychlorinated biphenyls

1. Introduction

Pollution of surface and ground water with higher chlorinated benzenes and polychlorinated biphenyls (PCBs) is not only of historical interest [1] but a still ongoing problem [2,3]. These compounds are ubiquitous in the environment nowadays due to their persistence in various environmental compartments and long-range transport in the atmosphere. Because of their bioaccumulative potential, toxic effects and indicator-function in emission control, they are considered as priority pollutants which have to be monitored [3,4]. In 1986, for example, the European Economic Community established as a quality target that the concentration of hexachlorobenzene in inland surface waters, estuary waters, internal coastal waters and territorial waters shall not exceed 0.03 μg/l [5]. Maximum permissible concentrations in drinking water have been also established, e.g. by German legislation with 0.5 μg/l for penta- and hexachlorobenzene and 0.1 μg/l for selected PCBs [6]. The monitoring of these substances in natural water samples can be a challenging task for analysts due to the complex and time consuming procedures for extraction, preconcentration, identification and quantification, especially at low concentration levels.

In recent years, much attention has been given to the minimization of sample preparation techniques, that could lead to solvent-reduced or solventless extraction, rapid and easy to handle procedures and on-line coupling. In this sense, several methods for environmental samples have been introduced, e.g. solid phase extraction [7], solid phase microextraction [8] and stir bar sorptive extraction [9].

As new extraction media, polymers like polydimethylsiloxane (PDMS) offered a big advantage over commonly adsorbent materials used in SPE, since they allow thermal desorption at lower temperatures leading to less sample degradation risks. Compared to other sorbents, PDMS shows inertness and good blank levels, and also discernible silicone degradation fragments from PDMS sorbent when using a mass selective detector [10]. The extraction of organic compounds from an aqueous phase with the sorbent

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PDMS was described by different groups in the mid-1980s using tubular traps coated with thick PDMS films. Practical disadvantages of this procedure were limited breakthrough capacities and the coupling to capillary chromatography after processing water samples due to the presence of residual water in the traps. SPME, another extraction technique that also employs PDMS among other materials, was proposed by Belardi and Pawliszyn [11] in 1989. It consisted of a quartz fiber coated with a polymeric layer, such as PDMS, which was retractable inside the needle of a syringe-like device. Different thickness and types of fiber materials are nowadays available [12]. The fiber can be exposed directly to the samples or used for headspace sampling. This easy-handling device allows on-line coupling with techniques such as GC. Despite of all these advantages, PDMS-SPME cannot though be considered as a universal technique since there are limitations regarding efficiency because of the small volume of PDMS coating (around 0.5 μl) [13]. Another possibility, in-tube SPME is a new effective sample preparation technique using an open tubular fused-silica capillary column (usually coated with PDMS) as an extraction device. Organic compounds in aqueous samples are directly extracted and concentrated into the stationary phase of capillary columns by repeated draw/eject cycles of sample solution, and they can be directly transferred to the liquid chromatographic column [14]. On-line in-tube SPME-performed continuous extraction, concentration, desorption, and injection using an autosampler, is usually used in combination with high-performance liquid chromatography and liquid chromatography–mass spectrometry. This technique has successfully been applied to the determination of various compounds such as pesticides, drugs, environmental pollutants, and food contaminants [15,16].

Another extraction technique was recently proposed which consisted of a short bed packed with PDMS particles [17]. Higher sensitivity was achieved when compared to PDMS-SPME, since it contained 300 μl of this material. A disadvantage of this technique was the drying step under a gas stream, required after processing aqueous samples, which can lead to loss of analytes.

The most recent of the above cited techniques using PDMS, SBSE, was suggested 4 years ago [18] as a simple and solventless technique and demonstrated for the enrichment of volatile and semivolatile micropollutants in aqueous samples [19]. It consists of a magnetic rod incorporated into a glass jacket, which is coated with a 0.5 mm layer of PDMS. This stir bar is then placed in the water sample and extraction is achieved during stirring. Since SBSE allows the use of a higher volume of PDMS in comparison to SPME, it has the advantage of higher sensitivity and thus more flexibility, showing good blank levels and no deterioration even after 100 extractions [9]. Interestingly, components with different polarities showed recoveries in a similar extent in SBSE, whereas in SPME the more apolar compounds are extracted in higher amounts than the least apolar ones [20]. Whereas SBSE might require a longer stirring period than SPME for full equilibration, this parameter is not essential for accurate quantification, although it might be desirable to approach the SBSE equilibrium extractable amount (PDMS saturation) and thus maximize sensitivity. In some cases, SPME might present better reproducibility results, since it can be coupled to an automatic sampler allowing on-line extraction.

The novel technique proposed here consists of a polydimethylsiloxane rod of, e.g. 8 cm length and 2 mm o.d., evaluated as an extraction medium for micropollutants in water. By shaking the sample solution containing the rod, the components are enriched in the PDMS phase. After this preconcentration step, the analytes are thermally desorbed from the rod on-line with GC–MS detection. Advantages of this approach are simplicity and low cost. Also, its easy handling is reinforced by the fact that no additional care during manipulation is required, since the PDMS rod does not require a supporting material, as is the case of the fiber in SPME and the glass jacket in SBSE, both fragile materials to a certain extent.

In this work, the novel technique was compared to SBSE for the analysis of priority selected chlorinated compounds in water. For this evaluation, water samples spiked with a mixture of six Ballschmitter and Zell [21] PCBs and two chlorobenzenes at the sub- and ng l^{-1} level were chosen.

2. Experimental

2.1. Chemicals

The solvents methanol, isooctane and dichloromethane were obtained in LiChrosolv quality from Merck. A 1 g l^{-1} stock solution mixture in methanol was prepared using pure solid standards of pentachlorobenzene, hexachlorobenzene and PCBs 28, 52, 101, 138, 153 and 180, purchased from Dr. Ehrenstorfer (Augsburg, Germany). These compounds, including the six Ballschmitter congeners [21] are depicted in Table 1. Milli-Q water was obtained by purification and deionization of tap water immediately prior to use with a Seralpur PRO 90 CN (Seral, Germany). The mixture containing the selected chlorinated compounds was used to spike 100 and 1000 ml water samples at the sub- and ng l^{-1} level.

2.2. Samplers: pretreatment, extraction and desorption

The commercial Twister™ stir bar for sorptive extraction was obtained from Gerstel (Mülheim an der Ruhr, Germany). It consists of a 1.5 cm length glass-encapsulated magnetic stir bar, externally coated with 24 μl of PDMS. Prior to first use, the stir bar was placed into a vial containing 1 ml of a mixture of methylene chloride–methanol (1:1) for 15 min. This procedure was repeated once more with a fresh mixture followed by a drying step using a lint-free tissue. The twister was then conditioned overnight at 250 °C with a nitrogen stream of 30 ml min^{-1}.

Table 1
Compounds of interest and specific ions used for MS identification and quantification

Peak number	Compound	Abbreviation	Structure	Ion 1	Ion 2
1	Pentachlorobenzene	PeCB	–	250	252
2	Hexachlorobenzene	HCB	–	284	142
3	PCB 28	PCB 28	2,4,4′-Trichlorobiphenyl	256	258
4	PCB 52	PCB 52	2,2′,5,5′-Tetrachlorobiphenyl	220	292
5	PCB 101	PCB 101	2,2′,4,5,5′-Pentachlorobiphenyl	326	254
6	PCB 153	PCB 153	2,2′,4,4′,5,5′-Hexachlorobiphenyl	360	362
7	PCB 138	PCB 138	2,2′,3,4,4′,5′-Hexachlorobiphenyl	360	290
8	PCB 180	PCB 180	2,2′,3,4,4′,5,5′-Heptachlorobiphenyl	394	396

To perform the extraction, the stir bar was introduced into a 100 ml Erlenmeyer or to a 1000 ml bottle containing the selected chlorinated compounds in aqueous media and submitted to a stirring speed of 2000 rpm (Variomag Multipoint 6/15, H + P Labortechnik, Oberschleissheim, München, Germany) or 150 rpm (for 1000 ml, since for higher stirring speed the twister movement became unstable) for a stipulated time. For direct comparison with the rod extraction method, a further procedure consisted of introducing the twister into a flask containing 1000 ml of the water sample spiked with the selected compounds mixture and submitted to a 360° shaker RA 20 (C. Gerhardt, Bonn, Germany) at 12 min^{-1} for a stipulated time. After that, the twister was removed from the solution with tweezers, dried with a lint-free tissue and inserted into the appropriated Gerstel thermal desorption glass tube (187 mm × 4 mm i.d.). The tube containing the twister was inserted in the thermal desorption unit, which consists of a rack with capacity for 20 tubes, available from Gerstel for automated analysis by thermodesorption GC–MS. Prior to use, the Gerstel glass tubes, used as a recipient for the samplers in the thermodesorption rack, were also treated with the 1:1 solvent mixture under sonication for 15 min. This procedure was repeated with a fresh mixture, followed by a drying step in a heating oven at 250 °C.

The newly proposed extraction approach consisted of a rod of PDMS (GoodFellow, Bad Nauheim, Germany) 8 cm long (0.2 cm o.d., mass ca. 300 mg), which corresponds to approximately 250 μl of PDMS. The length and diameter of the rod were chosen taking into consideration the dimensions of the TDS device, namely the heat zone length and the desorption tube i.d., respectively. Prior to first use, similarly to the twisters, a cleaning procedure was established, with the rod being placed into a vial containing 10 ml of the mixture of methylene chloride and methanol and horizontally shaken (HS501, IKA Labortechnik, Staufen, Germany) at 250 min^{-1} for 15 min. This procedure was repeated once more with a fresh mixture, followed by a drying step using a lint-free tissue. The rod was then conditioned overnight at 250 °C with a nitrogen stream of 30 ml min^{-1}. After this simple cleaning step, the same rod can be further used.

To perform the extraction, the rod was introduced into a flask or a bottle containing 100 or 1000 ml, respectively, of the water sample spiked with the selected compounds mixture and submitted to a 360° shaker RA 20 (C. Gerhardt) at 12 min^{-1} for a stipulated time. After that, the rod was removed from the solution with tweezers, dried with a lint-free tissue and inserted into the appropriated Gerstel glass tube for analysis by thermodesorption GC–MS.

2.3. Instrumental

Thermodesorption GC–MS of the selected chlorinated compounds sorbed in the twisters and rods was performed on an Agilent system (Agilent Technologies, Palo Alto, CA, USA) coupled to a Gerstel TDS A thermodesorption device. A cold injection system (CIS) using liquid nitrogen as a coolant consisted of an empty liner for cryofocusing the analytes prior to introduction into the capillary column.

The conditions utilized for the thermodesorption system were as follows: desorption temperature, 250 °C; desorption time, 10 min; and helium flow rate, 100 ml min^{-1} (solvent vent mode). The solvent vent mode is similar to the splitless mode, allowing the injection of much larger volumes as in the case of thermodesorption systems. Both transfer lines, situated between the thermodesorption device and the CIS, and between the GC and the MS detector were set at 250 °C.

The method utilized for the cold injection system was as follows: during thermal desorption, temperature set at −150 °C; heating at a rate of 12 °C s^{-1} to 250 °C (hold for 5 min); the injector was used in splitless mode with a splitless time of 1.5 min.

An HP-5 capillary column (30 m × 250 μm i.d., 0.25 μm film thickness) was used with a GC oven temperature program from 50 °C (3 min) to 160 °C at 15 °C min^{-1}, and to 250 °C at 3 °C min^{-1}. Helium was used as carrier gas with an average linear velocity of 40 cm s^{-1}. A detection method (5973 network MSD detector, Agilent) using the single-ion monitoring (SIM) mode which considered two characteristic ions for each compound was established for detection. The characteristic ions for each studied compound are shown in Table 1.

For detector external calibration, a 4 cm length plug of pesticide-grade glass wool (Supelco, Bellefonte, PA, USA) was placed inside of an empty Gerstel thermodesorption glass tube. One end of the plug was

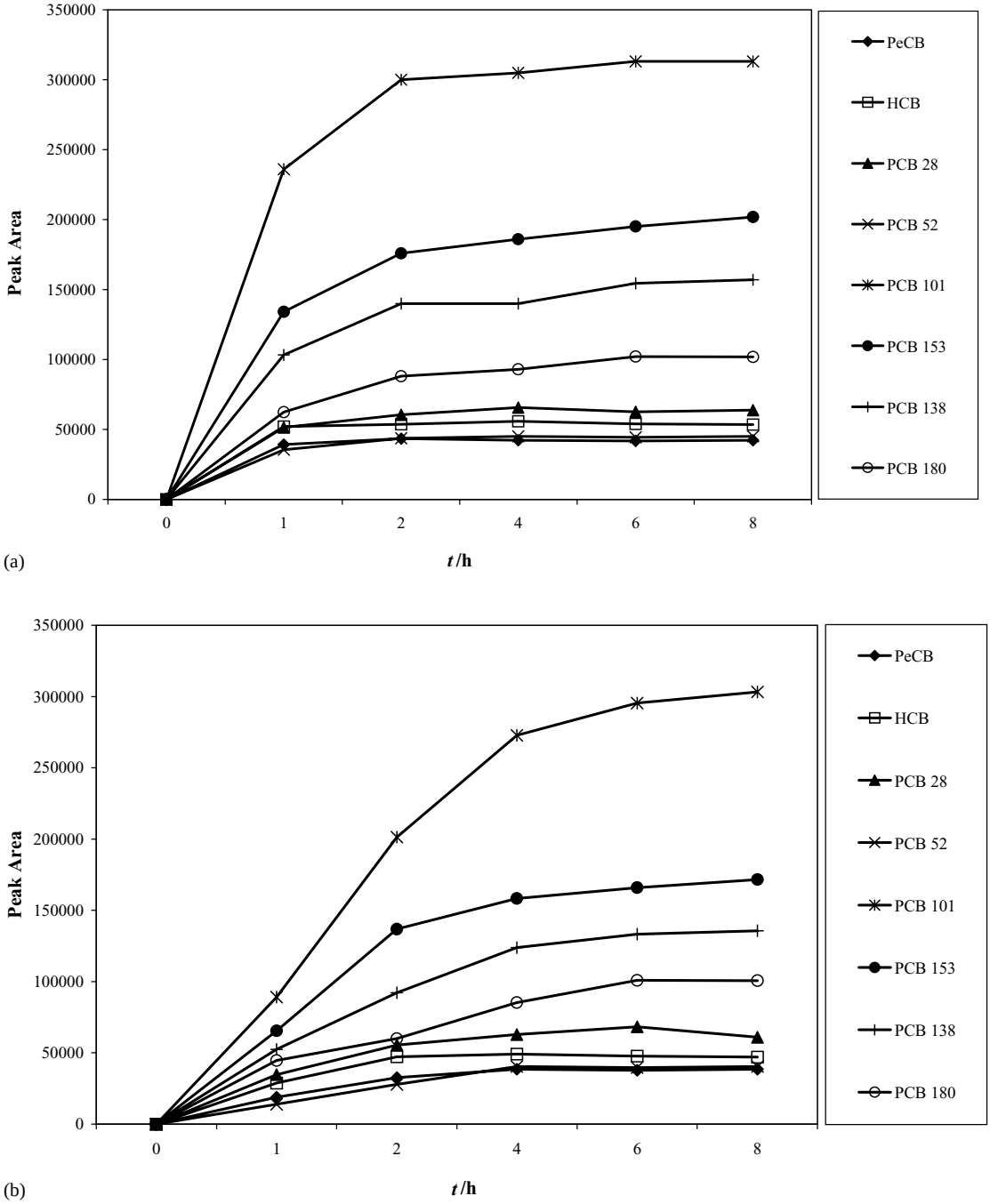
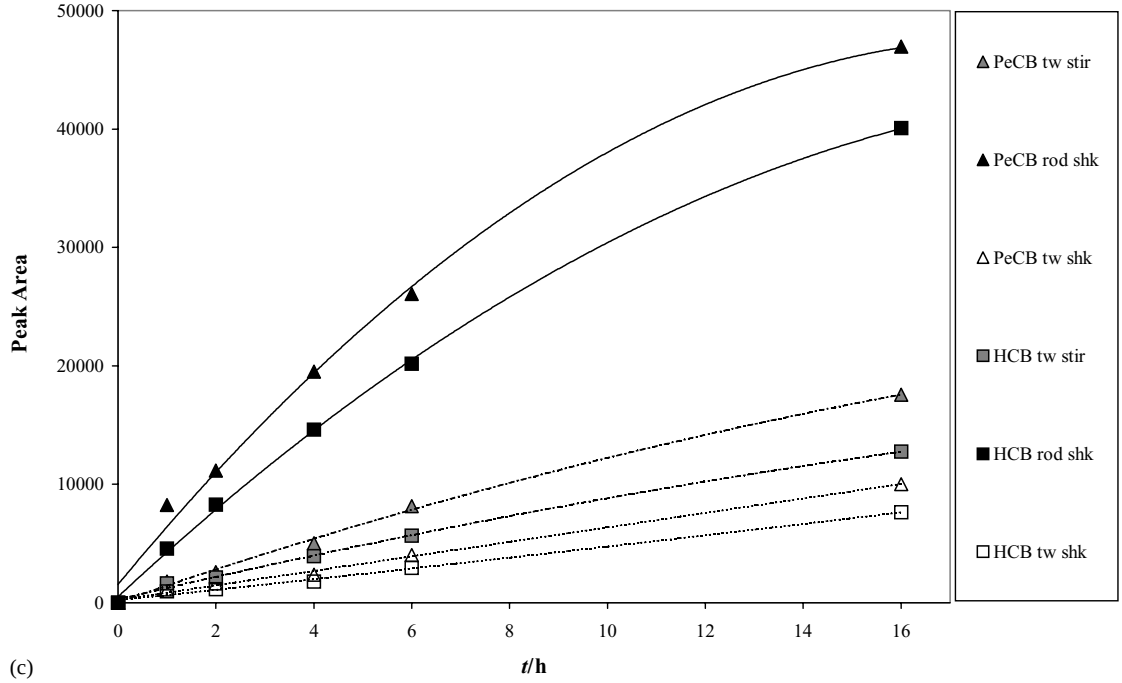
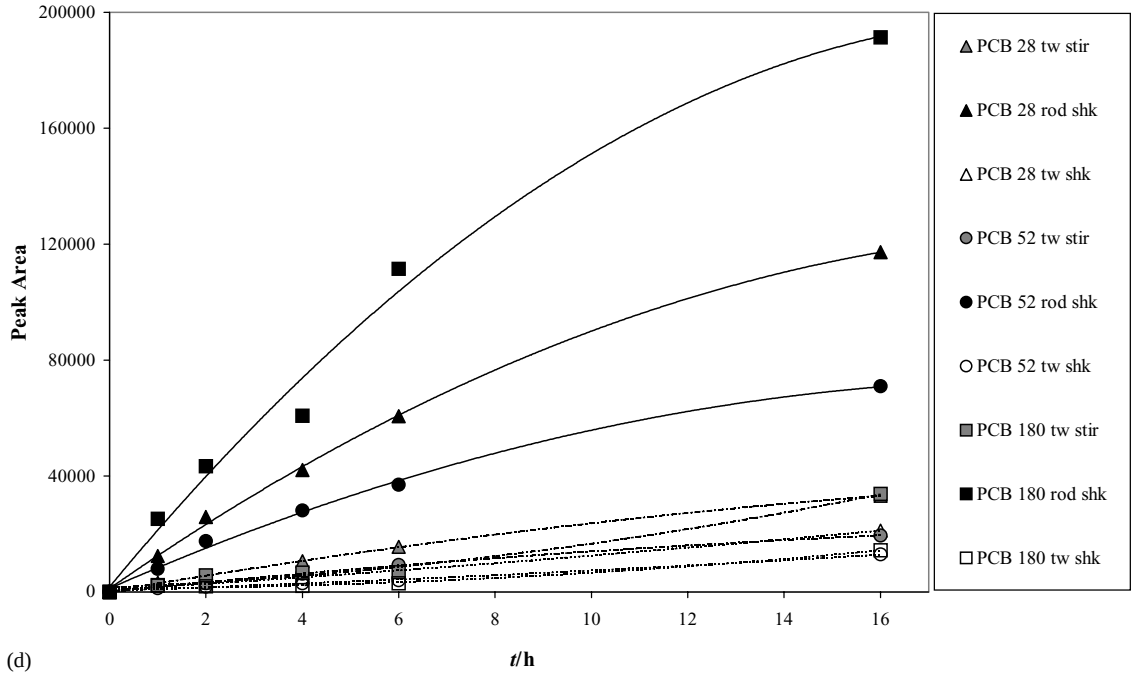


Fig. 1. (a) Extraction time profiles for the chlorinated compounds enriched in rods. (b) Extraction time profiles for the chlorinated compounds enriched in twisters. (c) Extraction time profiles for PeCB and HCB (0.2 ng l^{-1}) enriched in rods (shaking) and twisters (shaking and stirring), for 1000 ml water samples. (d) Extraction time profiles for PCBs 28, 52 and 180 (0.2 ng l^{-1}) enriched in rods (shaking) and twisters (shaking and stirring), for 1000 ml water samples. (e) Extraction time profiles for PCBs 101, 138 and 153 (0.2 ng l^{-1}) enriched in rods (shaking) and twisters (shaking and stirring), for 1000 ml water samples.

sealed with a metallic gauge stopper for desorption tube (Gerstel). This tube was then spiked with 1 μl of a standard solution containing the selected chlorinated compounds and connected to a cold injector (Gerstel) under 30 ml min^{-1} of nitrogen for 1 min to allow evaporation of the solvent (methanol). This tube was immediately transferred to the thermodesorption device (TDS A) for subsequent analysis. Using this procedure, a duplicate six-points external standard calibration curve (0.2–250 ng l^{-1}) was obtained for further quantification of the compounds enriched in the twisters and in the rods. The tubes filled with glass wool were also used in replicate for recovery studies (50 ng l^{-1}), following the same preparation procedure.



(c)

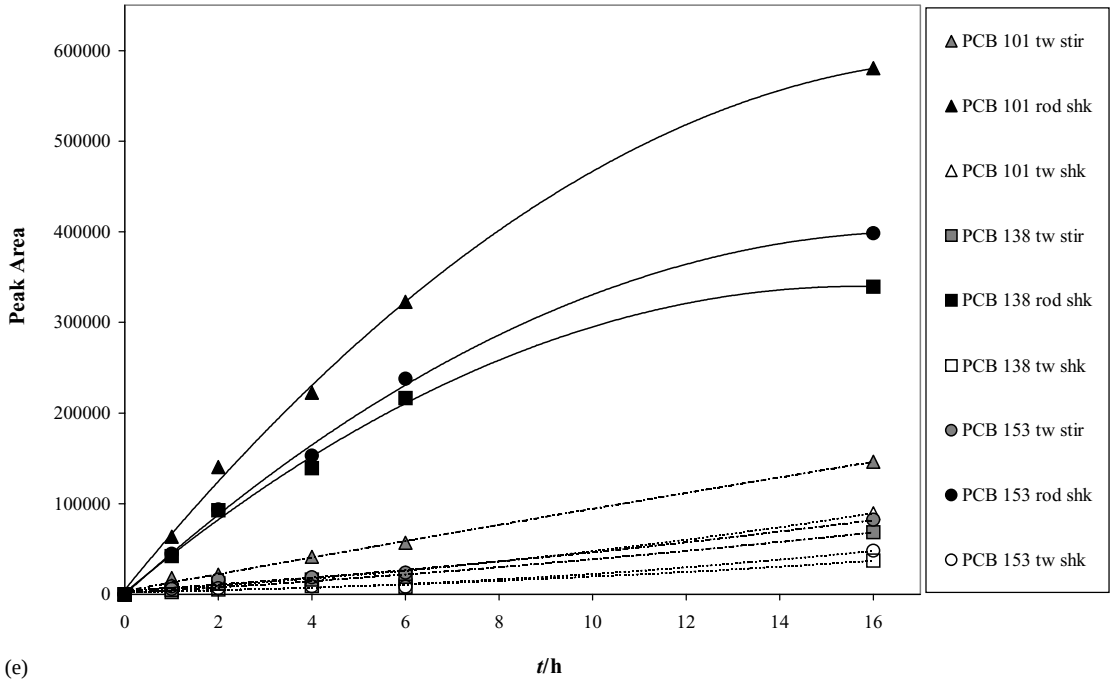


(d)

Fig. 1. (*Continued*)

2.4. Real sample

A sample of contaminated groundwater was analyzed using both twister and rod. The sample was obtained from the Bitterfeld site [22], Saxony-Anhalt, Germany, acidulated with HNO_3 until pH 2 and kept refrigerated at 10 °C. The original sample was filtered using an orange ring filter disc Celtron 30/0.45 μm (RC-GF92-TG100, Schleicher & Schuell, Dassel, Germany). Two aliquots of 100 ml were extracted in triplicate with twister and rod for 4 h. Thermodesorption and analysis were performed, the compounds were identified and quantified and the results for twisters and rods were compared.



(e)

Fig. 1. (*Continued*).

3. Results and discussion

3.1. Gas flow rate optimization during thermodesorption

The influence of TDS helium flow rates during thermodesorption was studied for rods and twisters at 50, 100 and 150 ml min^{-1}. It was observed that the variation of the gas flow rate has no significant influence on the desorption process and consequently on the signal intensity. For all the experiments, the flow rate was maintained at 100 ml min^{-1}.

3.2. Extraction time profiles

The extraction profile was investigated by enrichment of twisters (stirring) and rods (shaking) in 2 ng l^{-1} water samples (water volume of 100 ml) at extraction times of 1, 2, 4, 6 and 8 h. For a water volume of 1000 ml and analytes concentration of 0.2 ng l^{-1}, twister (stirring and shaking) and rod (shaking) extraction times were investigated for 1, 2, 4, 6 and 16 h. The curves obtained for the selected chlorinated compounds are shown in Fig. 1. In the case of the 100 ml flask, after 2 h of extraction, saturation of PDMS is already observed for rods, but for twisters it occurs only after 4 h. This is surprising but the cause may be that the PDMS surface for the rods (about 500 mm^2) is higher than for the twisters (about 80 mm^2). This finding gives opportunity to perform a faster extraction using the rods. To ensure that no exhaustive extraction takes place with the rods, another spiked sample (2 ng l^{-1} of each compound) was three times successively extracted with fresh rods, each rod being exposed to the solution for 2 h. The three rods were then thermodesorbed and analyzed. The peak areas corresponding to the three successive extractions were summed and considered hypothetically as 100%. For the investigated compounds, the first, second and third extraction corresponded to 75–87, 11–20 and 1–5% of the total peak area, respectively. These results confirm that for the studied conditions, the first rod did not perform an exhaustive extraction.

In the case of 1000 ml, after 16 h of extraction no equilibrium was observed for rods and twisters. The extraction is most efficient for the rods, followed by twisters stirred. A higher extraction yield for the twister could be supposedly reached if a higher stirring speed could be used. The efficiency of the shaking procedure for the twister is very poor.

3.3. Linearity

The linear range was investigated by exposing twisters and rods for 4 h to a batch of 100 ml water samples containing the compounds of interest at concentrations ranging from 1 to 250 ng l^{-1} (1.0, 2.0, 10.0, 50.0, 100.0 and 250.0 ng l^{-1}). Results for rods showed good linearity in this wide range ($r^2 = 0.992$–0.998). The linear range was also investigated by exposing rods for 16 h to a batch of 1000 ml water samples containing the compounds of interest at concentrations ranging from 0.05 to 50 ng l^{-1} (0.05, 0.2, 0.5, 1.0, 5.0, 10.0 and 50.0 ng l^{-1}). In this case, the curves for rods showed a likewise good linearity ($r^2 = 0.982$–0.999).

3.4. Limits of detection

To obtain the limit of detection (LOD) for the studied compounds (Table 2), three rods and twisters were exposed to pure 100 and 1000 ml water samples (not spiked with the

Table 2
Limits of detection (LODs) for the studied compounds with rods and twisters and concentration limits according to German Legislation for drinking water [6]

Compound	LOD ($ng\,l^{-1}$)			Drinking water limits ($ng\,l^{-1}$)
	Rods[a] (100 ml)	Twisters[a] (100 ml)	Rods[b] (1000 ml)	
PeCB	0.2	0.3	0.20	500
HCB	0.3	0.5	0.24	500
PCB 28	0.4	0.9	0.16	100[c]
PCB 52	0.6	1.5	0.17	100[c]
PCB 101	0.2	0.5	0.07	100[c]
PCB 153	0.3	0.6	0.02	100[c]
PCB 138	0.3	1.0	0.03	100[c]
PCB 180	0.5	1.8	0.03	100[c]

[a] Extraction time: 4 h.
[b] Extraction time: 16 h.
[c] Total PCB concentration limit: $0.0005\,mg\,l^{-1}$.

Table 3
Extraction efficiency for the studied compounds with rods and twisters for a 100 ml water sample

Compound	Rods		Twisters	
	Efficiency (%)	R.S.D.[a] (%)	Efficiency (%)	R.S.D.[a] (%)
PeCB	74.0	0.3	81.4	2.6
HCB	70.4	3.8	79.8	3.5
PCB 28	78.4	5.6	75.1	4.3
PCB 52	78.4	9.0	70.3	6.7
PCB 101	89.5	4.4	86.7	5.1
PCB 153	55.3	5.3	65.0	3.7
PCB 138	56.0	7.1	64.9	5.6
PCB 180	61.3	9.6	62.1	6.8

Extraction time: 4 h.
[a] Relative standard deviation for experiments carried out in triplicate.

selected chlorinated compounds) to obtain the blank values. For each compound, at the corresponding retention time no peak was found in the blank run. The limit of detection was therefore determined using the value corresponding to three times the standard deviation (S.D.) of the baseline noise. The LODs obtained here are 50–5000 times smaller than the German limits [6], as shown in Table 2. Extreme LODs were achieved with rods exposed to 1000 ml samples, although after 16 h of extraction the equilibrium was not reached.

3.5. Carry-over effects

To study the carry-over effect for each compound, three rods and twisters were enriched for 4 h in 100 ml water samples spiked with the selected chlorinated compounds to give an individual concentration of $50\,ng\,l^{-1}$, followed by thermodesorption. After that, a following second thermal desorption was carried out. Carry-over was calculated considering the chlorinated compounds percentage remaining

Table 4
Extraction efficiency for the studied compounds with rods (shaking) and twisters (shaking and stirring) for a 1000 ml water sample

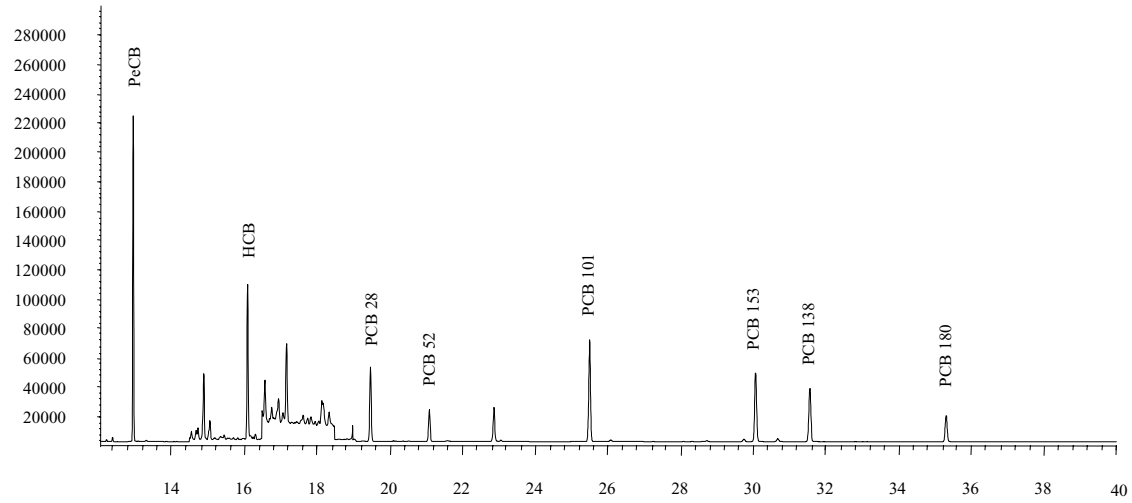
Compound	Rods shaking		Twisters shaking		Twisters stirring	
	Efficiency (%)	R.S.D.[a] (%)	Efficiency (%)	R.S.D.[a] (%)	Efficiency (%)	R.S.D.[a] (%)
PeCB	39.5	0.2	9.5	7.6	15.2	5.2
HCB	39.3	4.7	9.9	8.1	16.4	3.9
PCB 28	42.3	4.1	11.1	7.7	18.1	5.7
PCB 52	41.8	9.1	11.0	16.0	18.6	6.8
PCB 101	47.3	7.4	10.9	12.0	19.7	5.5
PCB 153	50.2	4.2	10.0	10.1	19.9	4.1
PCB 138	52.7	8.6	10.1	13.6	20.4	6.3
PCB 180	43.2	10.2	7.8	15.3	18.2	8.9

Extraction time: 16 h.
[a] Relative standard deviation for experiments carried out in triplicate.

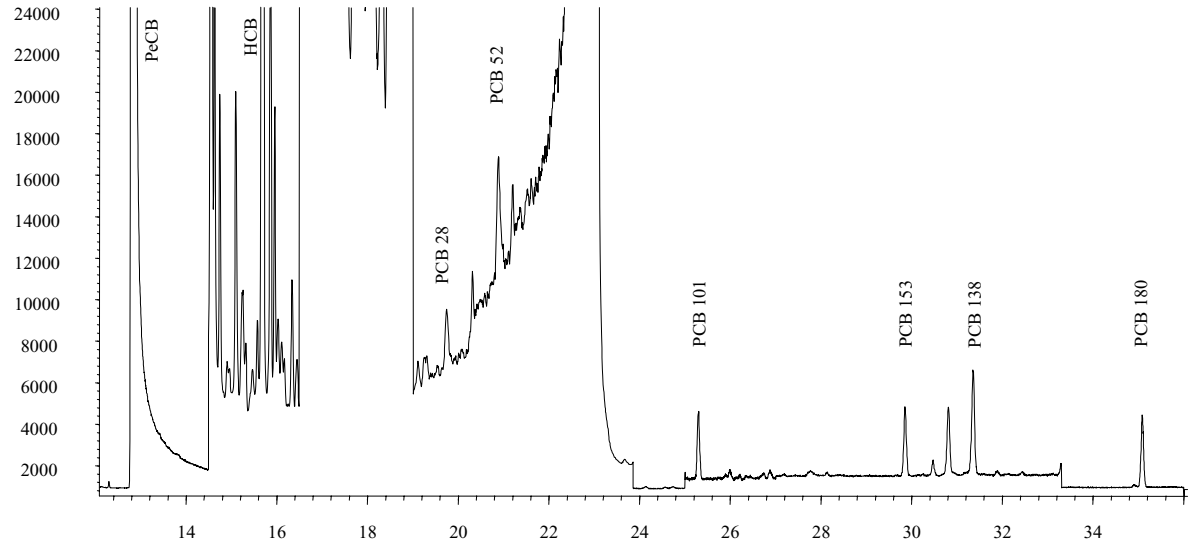
Table 5
Results obtained for the compounds of interest in a 100 ml ground water sample extracted with rods and twisters

Compound	Rods		Twisters		R.S.D.[a] (%)
	ng l^{-1}	R.S.D.[b] (%)	ng l^{-1}	R.S.D.[b] (%)	
PeCB	6057.1	5.9	6293.9	5.6	2.7
HCB	290.5	4.7	270.1	9.5	5.1
PCB 28	7.9	5.6	7.2	5.4	6.6
PCB 52	7.6	10.0	6.7	8.7	8.9
PCB 101	5.4	5.4	5.0	5.5	5.4
PCB 153	6.7	5.2	5.9	5.7	9.0
PCB 138	6.9	6.2	6.1	5.6	8.7
PCB 180	9.7	9.9	8.2	6.8	11.9

[a] Relative standard deviation between both methods (rod and twister extraction).
[b] Relative standard deviation for the analysis in triplicate.



(a)



(b)

Fig. 2. (a) Chromatogram obtained of a standard solution containing 50 ng of the chlorinated compounds extracted with rod. (b) Chromatogram of a water sample from Bitterfeld obtained after extraction with rod.

in the rods and twisters. It was observed that carry-over levels corresponded to 0.2–0.6% of the peak area found for twisters enrichment at 50 ng l^{-1} concentration, and to 0.6–6.4% of the peak area found for rods.

3.6. Extraction efficiency

To investigate extraction efficiency (Tables 3 and 4), rods and twisters were enriched for 4 h in a 100 ml water sample spiked with the selected chlorinated compounds to give a final concentration of 50 ng l^{-1}. Another procedure involved the extraction efficiency of rods and twisters (shaking and stirring) by enrichment for 16 h in a 1000 ml water sample spiked with the selected chlorinated compounds to give a final concentration of 50 ng l^{-1}. The extraction efficiency was calculated by comparing these results to the those obtained by thermodesorption of a glass wool tube spiked with a solution corresponding to 5 ng absolute weight (or 50 ng absolute weight for later comparison with 1000 ml samples) of each of the chlorinated compounds. Extraction efficiencies for rods were between 55 and 89%, and between 62 and 86% for twisters in 100 ml water samples. The fact that the extraction efficiencies of rods and twisters in the equilibrium do not differ significantly, although the rods contain about 10 times more PDMS material, could be associated with losses due to analyte glass adsorption in the flasks used, but further experiments to investigate this phenomenon are needed. Using 1000 ml water samples, the extraction yield of the rods was between 39.5 and 52.7%, and for the twisters (by slow stirring) between 15.2 and 20.4%, the equilibrium not being reached in both cases. Comparing the extraction efficiency of the rods for a 100 ml sample and a 1000 ml sample with the same concentration (50 ng l^{-1}) showed that, for the 1000 ml sample, the amount of compound absorbed is higher although the extraction efficiency is lower. For PCB 101, for example, 4.5 ng of the compound are extracted from a 100 ml sample, which corresponds to 23.7 ng of PCB extracted if a 1000 ml sample volume is used. This behavior can also explain the lower limits of detection found for rods in 1000 ml water sample.

3.7. Real sample analysis

Two aliquots of 100 ml ground water were extracted using rods and twisters (stirring) and the presence of the compounds of interest was investigated. Results for twisters and rods showed good agreement, as can be seen in Table 5. Fig. 2a and b show the chromatograms obtained after rod extraction of a standard solution and of the real sample.

4. Conclusion

PDMS polymers as an alternative material for extraction offer a big advantage over commonly sorbent materials, such as suitability for thermal desorption at lower temperatures leading to less sample degradation risks, inertness and good blank levels.

The PDMS rods presented above are a novel, simple and inexpensive approach to absorptive extraction of organic compounds from environmental samples. The new approach—as instrumentally compatible with thermodesorption as the twisters—was compared to the SBSE performance. It presented good linearity, blank levels and recoveries comparable to the stir bars, together with high sample capacity, simplicity, lower cost, less fragility and higher feasibility. Due to the high sample capacity, extremely low LODs can be reached (in the pg l^{-1} range). The extraction of a natural groundwater sample, compared with SBSE, illustrated its performance for the enrichment of the compounds of interest in water samples. Its main advantage over SBSE is the robustness and low cost, since the PDMS material in the twisters is supported by a glass jacket, which is fragile and breakable. Other special features of the material proposed here concern the flexibility by varying the length of the rod and also by dividing the rod in equal parts after extraction, which would allow replicates of the same sample. The use of solvent extraction as a substitute for thermodesorption could lead to instrumental simplification by coupling the PDMS rod extraction with simpler GC and HPLC injection ports/systems, or even by its application in bioassays. Further, the use of materials with different length and o.d. could present advantages regarding extraction time and efficiency. A possible feature of the new device proposed here is related to in situ sample extraction, which would avoid sample transport and storage in the laboratory until extraction.

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