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Review

# Silicone rod and silicone tube sorptive extraction

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ABSTRACT

This review focuses on the applications of silicone in the form of tubes or rods for sorptive extraction of organic compounds as sample preparation method in combination with various chromatographic techniques. Silicone rods (SRs) and silicone tubes (STs) have the advantage of being inexpensive, flexible and robust. SRs and STs with different sizes and volumes of silicone (8–635 μL) have so far been applied for the extraction/preconcentration of a large variety of organic micropollutants from different matrices. The theoretical principle of SR and ST extraction in comparison with similar microextraction techniques is presented as well as a summary of the published applications of SR and ST extraction in combination with gas chromatography (GC) or liquid chromatography (LC). Furthermore, the use of SRs and STs for time-integrated (passive) sampling is reported.



**Contents**



## 1. Introduction

In silicone-based extraction methods, polydimethylsiloxane (PDMS) is the most applied polymer. Using PDMS, the extraction rests upon the absorption of the analytes into the polymeric material [1]. Absorptive interactions are much weaker compared to adsorption on active surfaces. Therefore, analyte desorption can be performed under softer conditions, such as lower temperature and shorter desorption times and the degradation of unstable analytes is significantly less compared to adsorptive processes. Moreover, because the absorption into the bulk phase of PDMS (or more general the silicone phase) is the dominant partitioning process, no competition or displacement effects are expected among the multiple analytes which are extracted from the sample. PDMS provides several advantages, such as high stability towards temperature, water and a broad range of organic solvents. Degradation products of PDMS are very specific and can be easily determined with a mass selective detector.

First applications using PDMS as sorptive extraction phase were performed in the 1980s. Organic substances were extracted from

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water and trapped in an open-tubular capillary column coated with cross-linked PDMS. After a drying step the analytes were analysed by thermodesorption (TD) and GC [2,3]. In 1989 solid phase microextraction (SPME) has been developed [4–6]. SPME uses a short piece of a fused-silica fibre coated with a polymeric stationary phase. The SPME fibre is exposed to the liquid sample or to the headspace (HS) of the sample. After the extraction, desorption is performed either thermally (in combination with GC) or with a small amount of solvent [6]. This easy-handling device offers on-line combination with GC. In the following years (1995–2000) special designed interfaces for LC combination were developed [7–10]. One modification, called in-tube SPME is a technique using an open-tubular fused-silica capillary column (usually coated with PDMS) as extraction device. The analytes in aqueous samples are directly extracted and concentrated onto the stationary phase of capillary columns by repeated draw-and-eject cycles of the sample solution, and they can be directly transferred to the liquid chromatographic column [11]. With on-line in-tube SPME continuous extraction, desorption, and injection can be performed using an autosampler. On-line in-tube SPME is usually used in combination with LC and LC–MS and has successfully been applied to the determination of a large variety of compounds such as drugs, pesticides, food contaminants and environmental pollutants [12,13]. The SPME technique has developed very fast and in the last 20 years hundreds of publications applying SPME in environmental, food, medical and forensic fields have been published (with a steady increase). In 2006 SPME was included in a standardised norm (DIN) as a possibility to determine pesticides with GC–MS analysis [14]. Despite all these benefits SPME includes some limitations such as the fragile nature of the fibre [15] and the limited extraction efficiency of SPME due to the small PDMS volume (ca. 0.5 μL) [16]. Another approach that uses higher amounts of silicone is solid phase dynamic extraction (SPDE) where the inside of a needle is coated with PDMS and additives (50 μm film thickness and 56 mm film length) and the HS of a sample is extracted performing numerous extraction cycles. SPDE is also a commercial device and has successfully been applied for the extraction of volatile organic compounds (VOCs) [17,18]. Besides pure PDMS, other coatings such as polyethylene glycol (WAX), cyanopropylphenyl/PDMS and PDMS/activated carbon are applied in SPDE [17]. Also, very high sensitivity is achieved with a technique using PDMS particles (300 μL) packed in a short bed that was introduced by Baltussen et al. [19]. The analytes are extracted into the packed bed followed by thermal desorption enabling complete transfer of the enriched solutes onto the GC column. A disadvantage of this technique is the required drying step under a gas stream that can lead to analyte losses. Another very successful approach to overcome some of the limitations of the existing techniques, such as the low recovery achievable with SPME, is stir bar sorptive extraction (SBSE) introduced by Baltussen et al. in 1999 [20]. SBSE is based upon sorption of the analytes onto a film of PDMS (same principle as SPME) coated onto a glass-coated magnetic stir bar. The stir bar is commercialized as Twister and provided by Gerstel GmbH, Mülheim, Germany. The volumes of PDMS are much higher compared to SPME, allowing higher analyte enrichment. Four different stir bars with volumes of 24 μL, 63 μL, 47 μL and 126 μL are to date commercially available [21]. Mostly SBSE is combined with thermal desorption but solvent desorption is possible as well [22] giving the possibility for replicate analysis and LC combination. SBSE was first applied to direct aqueous sampling but later extended to headspace sampling [23]. Diverse applications in different fields of analytical sampling including sampling from biological fluids [24] are described in several reviews [25–27]. As SPME, SBSE is a microextraction device with continuously increasing interest and more that 300 publications are already published since 1999 [27].

PDMS as extraction medium is also available in manifold non-commercialized designs and has been described in several applications during the last years. For example, thin films of PDMS (thin film microextraction) are put inside a sample container, either directly in the sample or in the headspace [28]. After extraction the PDMS sheet is rolled around a rod and placed in the GC injector (in the centre of the glass liner) to perform thermal desorption. Some applications describe the usage of silicone materials as sheets in passive sampling devices for the determination of partition coefficients [29,30] and toxicity tests [31]. Moreover, silicone coatings to caps, pipette tips, and well plates or to walls of vials are also used in sample preparation for chromatographic analysis and are introduced, e.g. under the trademark “Immobilized Liquid Extraction” by Wohleb in 2003 [32] or as “Sorptive Layer Vial Extraction” by Frank and Guan in 2004 [33].

Another not yet commercialized technique is the silicone rod (SR) and silicone tube (ST) sorptive extraction. Similar to the commercialized Twister, in 2004, Popp et al. started to employ silicone materials in form of rods and tubes for the enrichment of organic compounds [34,35]. In terms of analyte extractions the SRs and STs are similar to SPME and SBSE but with the advantage of being inexpensive, flexible and robust. SRs and STs with different sizes and phase volumes (8–635 μL) have been applied for the extraction of a large variety of organic micropollutants. This review focuses on the applications of silicone materials in the form of tubes or rods applied for extraction, desorption and following GC or LC analysis and in passive sampling. Some of the presented materials consist of pure PDMS, but most of them are described in the corresponding literature as silicone or polysiloxane materials consisting of PDMS with some additives. For example, the STs provided by Reichelt Chemietechnik GmbH (Heidelberg, Germany) consist to only 70% of PDMS. Other constituents such as silicic acid esters are added as fillers. Also the SR sold by the metre as flexible rod (of 1 mm or 2 mm diameter) by Goodfellow (Bad Nauheim, Germany) is not pure PDMS but a phenyl-vinyl-methyl polysiloxane (a so-called PVMQ silicone rubber) which has some filler like chalk.

## 2. Theoretical principles of silicone-based sorptive extraction

In silicone-based extraction processes, the partitioning of the analytes takes place between the sample (mostly aqueous or gaseous) and the polymeric phase. The knowledge of the distribution coefficients is important for the estimation of the analyte partitioning and for the calculation of the recovery. In the following equation, the analyte partition between two non-miscible phases (an aqueous sample and a polymeric extraction phase) is described.

$$R = \frac{m_s}{m_0} = \frac{K_{sw}/\beta}{1 + (K_{sw}/\beta)} = \frac{1}{(\beta/K_{sw}) + 1} \quad (1)$$

where $R$ is the recovery or extraction yield, $m_s$ the mass of analyte in the silicone phase, $m_0$ the total mass of analyte, initially only present in the water sample, $K_{sw}$ the partition coefficient between silicone phase and water, $\beta$ the phase ratio ($=V_w/V_s$, with $V_s$ as volume of silicone phase and $V_w$ as volume of water phase). Eq. (1) shows that the recovery depends on both, the values of $\beta$ and $K_{sw}$. The $K_{sw}$ value is often approximated by the well-known octanol–water partition coefficient $K_{ow}$ [25,36,37]. Recently, more sophisticated approaches are used for the analysis and prediction of sorption coefficients (like $K_{sw}$). One of the most useful approaches is the solvation parameter model of Abraham [38] which has recently been applied for the sorption of gaseous and organic solutes onto PDMS-coatings of SPME fibres [39,40]. High $\beta$ values, resulting from a small volume of the extraction phase compared to the aqueous phase, led in combination with lower and moderate partition coefficients to a low recovery. For very high partition coefficients, the

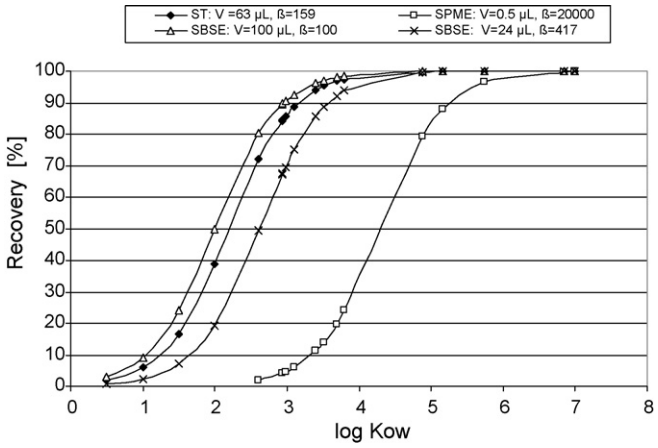


**Fig. 1.** Recovery for SBSE, SPME and ST extraction under equilibrium conditions, calculated for an aqueous sample volume of 10 mL and the corresponding silicone volume.

phase ratio does not influence the recovery. In such cases almost quantitative extraction is achieved. The higher sensitivity of SBSE compared to SPME concerning analytes with a small log $K_{ow}$ value is often emphasized. For comparing the SR and ST extraction with SPME and SBSE, the theoretical recovery values for these three techniques in dependence of the log $K_{ow}$ value are shown in Fig. 1. The calculations are based on equilibrium conditions, a sample volume of 10 mL, and a silicone phase of 0.5 μL for SPME, 24 μL and 100 μL for SBSE, and 63 μL for the ST extraction, which was for example used in Ref. [41]. Fig. 1 demonstrates similar recoveries for SBSE and ST extraction. Both techniques have a high capacity and allow an exhaustive extraction for analytes with log $K_{ow} > 5$. Compared to SPME (with PDMS fibre), the higher recovery for analytes with log $K_{ow} < 4$ is pointed out. These aspects underline the high extraction potential of SBSE and ST/SR extraction for a sensitive determination of analytes in a broad range of polarity.

## 3. Practical aspects of SR and ST extraction and processing

### 3.1. Extraction

The extraction procedure using SRs and STs is similar to SBSE and very simple to apply. Several types of SRs and STs are shown in Fig. 2 and a general scheme of the extraction and desorption procedure is presented in Fig. 3. The SRs and STs are available by different suppliers (listed in Tables 1 and 2) as yard ware. In the laboratory they are cut in pieces and mostly weighted before application to ensure that each time the same volume is used. Generally, only the pieces with a deviation below 10% are employed. Before application they undergo a cleaning step, either thermally (heating overnight in a stream of nitrogen) or with a solvent. For extraction, the SR or ST is put into the liquid sample and shaken for a definite time. Another possibility is hanging the material in the HS above the sample which is favourable for the STs, as they can easily be put on a glass- or steel adapter (see Fig. 2 and [42]). The extraction times to reach equilibrium are very different and depend on the applied sample and silicone volume as well as on the analytes. It is possible to work under non-equilibrium conditions when all other parameters are kept constant [35]. In passive sampling, the devices containing SRs or STs are exposed to the sampling site for a certain period of time (weeks or months). After sampling, the passive sampler is brought into the laboratory and desorption of the analytes is performed (same way as presented in Fig. 3).

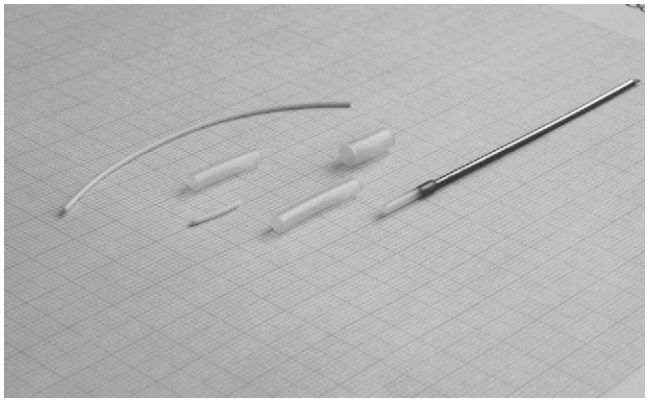

**Fig. 2.** Different dimensions of SRs and STs, achieved from Goodfellow and Reichelt Chemietechnik GmbH.

### 3.2. Processing

#### 3.2.1. Thermal desorption

In most applications ST and SR extraction is combined with thermal desorption as a solvent-free, automated approach with enhanced sample capacity. The disadvantage of being a "one shot" technique can be overcome as dividing the material before desorption is possible, which allows replicate analysis. Thermodesorption can lead to enhanced material degradation which has to be considered carefully. Although the silicone material is relatively stable towards high temperatures, degradation products can be found in the chromatograms. A comparison of blank rods and blank Twisters after thermal desorption is shown in Fig. 4. Using both materials some background peaks are present in the scan chromatograms. Using the rods, the background noise is higher, showing, that this material is not as clean as the Twisters. The compounds are to the main part silicone components and also phthalates and alkanes. These peaks are attributed to the chemical composition of the materials. In contrast to the Twisters, that consist of pure PDMS, the STs and SRs contain besides PDMS also other constituents (as mentioned in the introduction part and for example in Ref. [41]). But several applications showed, that using single ion monitoring (SIM)-mode these interfering peaks can easily be masked [41,42]. Batch to batch reproducibility using SRs and STs is an important question and previous applications indicated good reproducibility with precision values around 10% RSD for PCBs and chlorobenzenes [35,42]. Still, further detailed investigations on the material from different batches and suppliers are necessary.

#### 3.2.2. Solvent back-extraction

Back-extraction of the SRs and STs with solvents is possible as well. Different kinds of solvents can be applied. Rusina et al. [43] investigated the swelling behaviour of (among others) SRs in different solvents. They found that swelling decreased in the order: hexane > dichloromethane > ethyl acetate > acetone > methanol. The more the material swelled the more breakable it became, but all materials regained their original size after solvent evaporation. From these investigations methanol seems to be a very suitable desorption solvent being conveniently combinable with LC-analyses [37]. But also the usage of non-polar solvents (cyclohexane, ethyl acetate) is possible as the swelling of the material does not seem to affect their desorption characteristics [41]. As the material is usually used only once long-term stability is not required. Applying solvent back-extraction, the material decomposition is reduced compared to thermodesorption. GC–MS chromatograms (in scan mode) of ethyl acetate and cyclohexane after back-extraction of ST pieces contain fewer material (background) peaks and causes no serious peak interferences with target analytes (Fig. 5).

**Table 1**
SR/ST applications to extract organic compounds from samples of different aqueous matrices and air.

| Analyte | Matrix | Extraction technique | Silicone volume | Sample volume | Extraction time | Desorption + analysis | LODs | Silicone supplier | Additional | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| PAHs | Water | Direct with SRs | 8 μL | 15 mL | 180 min | Solvent-LC–FLD | 0.1–1.2 ng/L | Goodfellow | | [34] |
| PCBs, chlorobenzenes | Water | Direct with SRs | 250 μL | 100–1000 mL | 4–16 h | TD–GC–MS | 0.02–0.6 ng/L | Goodfellow | Comparison with SBSE | [35] |
| Pharmaceuticals | Water | Direct with SRs | 62 μL | 480 mL | 1–34 days | Solvent-LC–MS | 3–16 μg/L | Goodfellow | Determination of $K_{sw}$ values | [37] |
| Pesticides | Water | Direct with STs | 63 μL | 10 mL | 40 min | Solvent-GC–MS (large volume injection) | 0.1–5 ng/L | Reichelt Chemietechnik GmbH | | [41] |
| Chlorobenzenes | Water | HS with STs | 35 μL | 50 mL | 60 min | TD–GC–MS | 2–12 ng/L | Reichelt Chemietechnik GmbH | Comparison with SBSE | [42] |
| Polybrominated diphenyl ethers | Water | HS and direct with SRs | 31 μL | 80 mL | 14 h | Solvent-GC–ECD | Low ng/L | Goodfellow | | [45] |
| Halogenated anisoles | Water, wine | HS and direct with SRs | 31 μL | 80 mL | 150 min | Solvent-GC–ECD or GC–MS/MS | LOQ: 0.5–20 ng/L | Goodfellow | | [46] |
| Organophosphorus pesticides | Water | Direct with SRs | 47 μL | 100 mL | 180 min | TD–GC–MS | 0.01–0.45 ng/L | Goodfellow | Comparisson with SBSE | [47] |
| 44 hazardous compounds (PAHs, chlorobenzenes, phthalates) | Water, snow | Direct with STs (HCSP) | 120 μL | 100 mL | 1 h (non-equilibrium) | TD–GC–MS | 0.02–0.078 ng/L (PAHs) | Bibby Sterlin, Stone, UK | Changes to the injector hardware | [51] |
| VOCs, PAHs, phthalates | Water, rooibos tea | HS with STs (SEP) | 24 μL | Not given | 10 min to 24 h | TDS–GC–FID | Not given | Mueller Labor Betrieb, Heidelberg | Changes to the injector hardware | [52] |
| Aromatic compounds (toluene, 1,2,4-trimethylbenzene, a-methylstyrene, PAHs) | Air | Direct with STs (multi-channel thick film traps) | 635 μL | 140 mL | 10 min air flow on the tubes | TDS–GC–MS | Sub ppb | Silastic, medical grade tubing, Dow Corning, Midlands, MI, USA) | Several STs are filled in a TD glass tube | [53] |
| Aroma compounds | Milk | HS with several STs (MCTs) | 635 μL | 200 mL | 25 min | TDS–GC–FID | LOQ: 0.6–13 μg/L | Silastic, medical grade tubing, Dow Corning | Several STs are filled in a TD glass tube | [54] |

**Table 2**
SR/ST as (part of) passive sampling devices for water and air monitoring.

| Analyte | Sample matrix | Exposue mode | Silicone volume | Exposure time | Desorption + analysis | LODs | Silicone supplier | Additional | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Semivolative organic pollutants (chlorobenzenes, HCHs, DDE, PAHs) | Water | SRs and STs + water in LDPE tubing (MESCO) | 250 μL | 2 weeks–several months | TD–GC–MS | ng/L to pg/L | SRs from Goodfellow STs from Reichelt Chemietechnik GmbH | Comparison with Twister as receiving phase | [60] |
| Chlorinated organic compounds (chlorobenzenes, HCHs, PCBs) and PAHs | Water | SRs + air in LDPE tubing (MESCO) | 47 μL | 28 days | TD–GC–MS | Not given | Goodfellow | | [61] |
| PAHs, PCBs, HCB, DDE | Water | SRs and MESCOs + water | 160–470 μL | 7–28 days | TD–GC–MS | ng/L to pg/L | Goodfellow | Spiking with PRCs, comparison with SPMDs, Chemcatcher, silicone strips and LDPE-membranes | [62] |
| Selected PAHs and chlorinated hydrocarbons chlorinated organic compounds (chlorobenzenes, HCHs, PCBs) and PAHs | Water | SR + water | 250 μL | 22–28 days | TD–GC–MS | Not given | Goodfellow | Spiking with PRCs | [67] |
| PAHs | Water | SR rods (on-rod-sampling) | 8 μL | 1 month | TD–GC–MS | Not given | Supelco,Oakville, Canada | Comparison with direct SPME | [69] |
| Semivolative organic pollutants (HCHs, PCBs) | Air | STs + air in LDPE tubing (MESCO) | 250 μL | 28 days | TD–GC–MS | Not given | Reichelt Chemietechnik GmbH | Comparison with Twister as receiving phase | [64] |
| Chlorinated semi-volatiles (HCB, HCHs, PCBs) | Air | SRs (spiral-rod sampler) + air in LDPE tubing (MESCO) | 124 μL | 168–504 hours | TD–GC–MS | Not given | Goodfellow | Comparison with Twister as receiving phase | [65] |

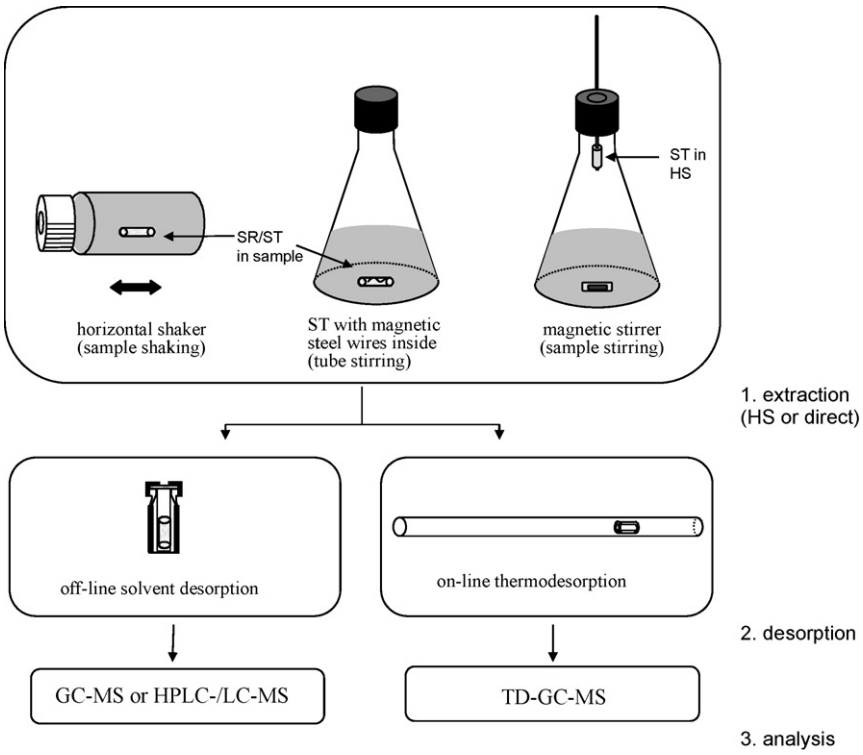


**Fig. 3.** Scheme of SR and ST extraction and processing.

In using GC-compatible solvents for the back-extraction of ST/SR which cause considerable swelling of the silicone one should bear in mind that the portion of solvent remaining in the silicone material does absorb a certain part of analytes, which is not accessible to further analysis. This can be critical in extreme trace analysis but can partly be counteracted by using larger solvent volumes and/or repeated extraction. The (unified) extract has to be concentrated then before GC analysis or large volume injection (LVI) should be applied.

## 4. Applications

### 4.1. SR and ST extraction for analytical sample preparation

The idea using SRs and STs for the extraction arrived when Popp et al. published a method for the determination of PAHs in water samples applying SBSE and LC–FLD [44]. After this successful application, in 2004 they applied the same method and exchanged the Twister by a SR [34]. They found the SRs to provide same advantages

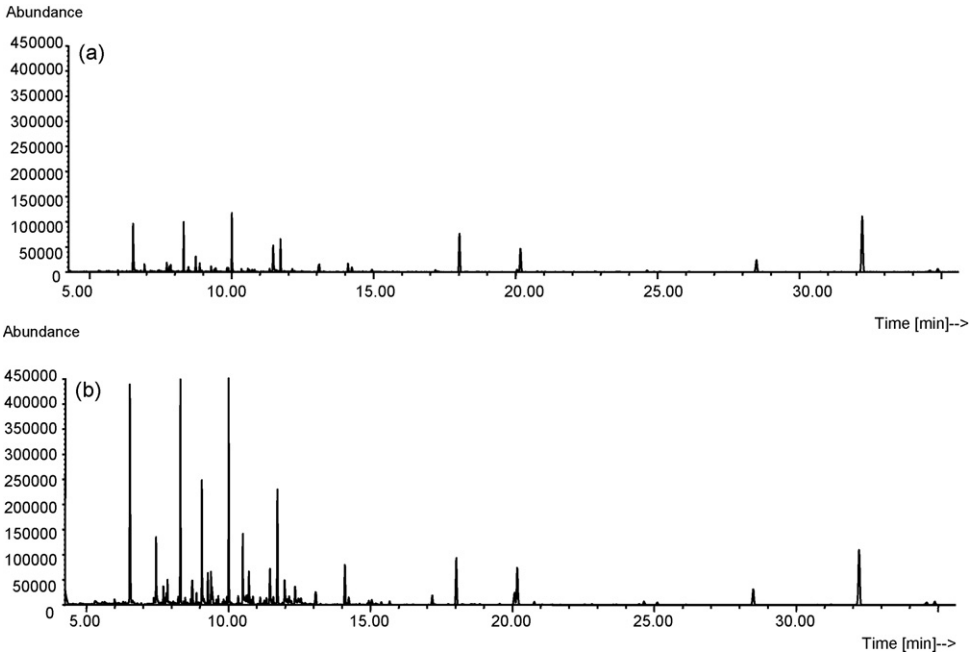


**Fig. 4.** Scan chromatograms of (a) a blank stir bar (from Gerstel) and (b) a blank SR (from Goodfellow) after thermodesorption–GC–MS analysis (TD: 250 °C, 5 min, 50 mL/min).

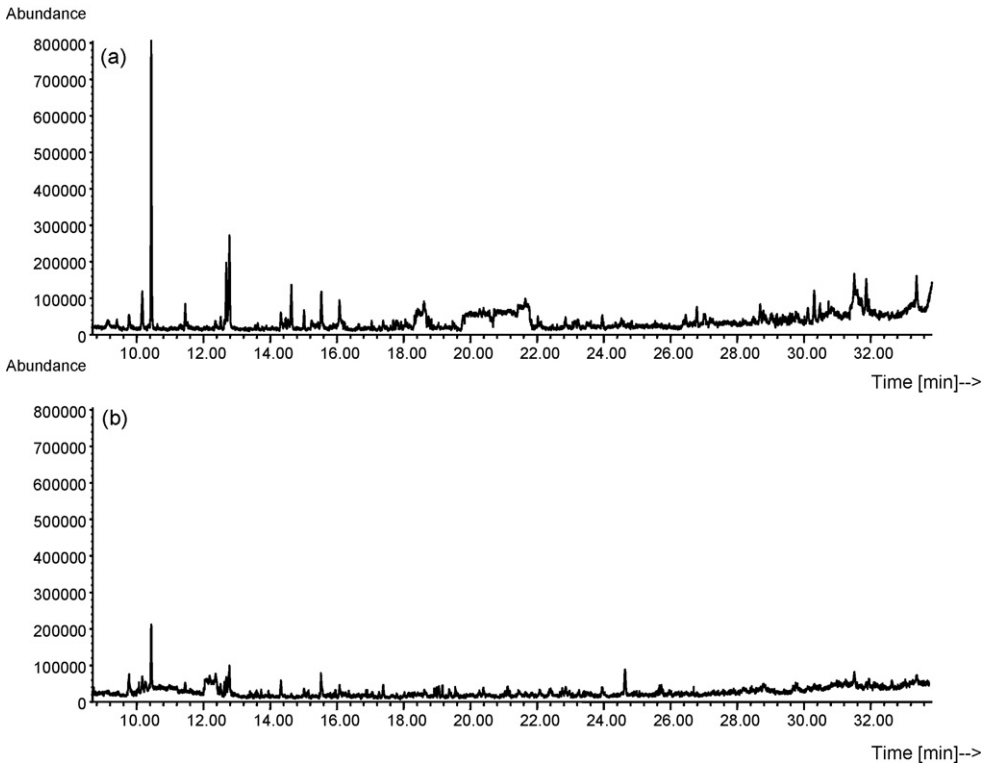


**Fig. 5.** Scan chromatograms of blank STs (from Reichelt Chemietechnik GmbH) using (a) cyclohexane and (b) ethyl acetate as desorption solvent, 15 min desorption time, analysis: large-volume-injection–GC–MS.

as the Twisters (in terms of handling, sensitivity and reproducibility of the materials) with the advantage of having an inexpensive, single-use and high flexible extraction material. In a later application of the same group, SRs were used for extraction of PCBs and chlorobenzenes from water in combination with TD–GC–MS [35]. Here, a direct comparison between the Twister and SRs led to similar recoveries, precision values, and detection limits (LODs) for the target analytes. A recently published application showed headspace (HS) extraction of chlorobenzenes from water samples providing similar extraction efficiencies of ST pieces compared to the Twister (using a similar silicone volume) [42]. Generally the advantage of the STs and SRs is their low cost (ca. 5 cent per piece). Therefore they can be discarded after a single use, eliminating carry-over problems. Moreover, the extraction material can easily be adjusted to specific needs of an extraction task, by varying the length and thickness of the rods and tubes to address different sample volumes and analyte concentrations. Therefore the applications range is hardly limited because SRs and STs are available in numerous lengths, thicknesses and with different diameters. For example, SRs with a volume of approximately 8 μL were used for the extraction of PAHs [34] and 250 μL SRs (8 cm long) were applied for a very sensitive extraction of PCBs and chlorobenzenes [35]. Montes et al. applied SRs for direct and HS extraction of polybrominated diphenyl ethers and halogenated anisoles from water and wine samples [45,46]. Moreover, SRs and STs have been used for pesticide enrichment [47,41]. In some applications the long-term stability of the analytes in the materials was investigated. It was found that after enrichment the materials can be stored in the fridge and the analytes stay stable for 24 h (tested for pesticides ([41]) and for 2 weeks (tested for anisoles [46]). A general difference among SRs and STs is the faster equilibration using STs in contrast to SRs (and the Twisters) attributed to the higher surface of the STs [41].

In another study SRs were applied for the enrichment of polar pharmaceuticals from water with time-resolved batch extraction tests [37]. The analytes were desorbed with methanol and analysis was performed with LC–MS. The $K_{sw}$ values of the pharmaceuticals under investigation were determined. It was found that enrichment of these polar pharmaceuticals in the SRs is lower compared to other compound classes (such as PAHs and chlorinated hydrocarbons) which is attributed to the fact that the enrichment is strongly related to the hydrophobic character of the compounds. Moreover, the practical LOQ values were considerably higher for ionisable compounds because only the non-dissociated forms seem to be taken up by the SR as it is generally assumed for the interpretation of partitioning phenomena [48]. If, in contrast to Ref. [37], extraction is performed under depletive conditions (i.e. using a small phase ratio), lower LOQ can be reached due to the continuous disturbance of dissociation equilibrium in sample solution. (The adjustment of sample pH is another common method to shift dissociation equilibria of analytes.)

Recently, direct SR extraction of PAHs from soil leachates followed by TD–GC–MS was tested against other microextraction techniques (SPME fibre coated with 100 μm PDMS from Supelco (Bellefonte, PA); Twister bar of 1 cm length coated with 0.5 mm PDMS from Gerstel) and the conventional liquid–liquid extraction followed by HPLC-FLD as reference method [49]. Applying external calibration procedures for each method (with 12–15 concentration levels in the ng/L to μg/L range), no significant differences could be found between the leachate concentrations determined for the 2–4-ring PAHs. The results also met the overall mean values obtained in a ring test with 14 participating laboratories within the limits of the respective standard deviations. Hence, SRs can be seen as a promising and inexpensive tool for solvent-reduced sample preparation in soil/waste leaching tests. Moreover, work is in progress on the validation of SR pieces as tool for (biomimetic) in situ extraction of persistent organic compounds in soil/waste leaching tests. Recently, SR pieces were successfully tested to quantify the internal dose of a chemical in zebrafish eggs [50]. This demonstrates the potential of SR extraction even with small sample volumes normally used in *in vitro* bioassays.

Other authors applied STs for systems with modification of the injector hardware. The aim was the possibility of direct desorption of the STs in the injector (equivalent to direct SPME desorption in a conventional injector) allowing on-line GC combination. Pettersson et al. [51] applied STs for sorptive extraction of water samples using silicone rubber with a volume of 122 μL. The so-called high capacity sorption probe (HCSP) was immersed into the aqueous sample and after analyte enrichment desorption was carried out by a robotic autoinjector into the modified injector of the GC. As the setup is fully automated, unattended and precise time-controlled extraction of samples is possible and allows quantitation under non-equilibrium conditions. The system was evaluated with a test mixture of 44 environmentally hazardous compounds. A similar injector-adapted system was described by Burger et al. [52]. They applied sample enrichment probe (SEP) using STs with a volume of ca. 25 μL attached to a stainless steel rod. This device was put into the headspace of the sample and after some changes to the injector hardware (e.g. enlarging the needle guiding channels and the septum-supporting insert), direct thermal desorption into the GC was performed. For the introduction and removal of the SEP the injector was opened to the atmosphere. For the determination of volatile and semi-volatile organic compounds in gaseous and aqueous media, the SEP technique gave results comparable with those obtained by the SBSE and HCSP. Implementation of the SEP technique requires minor adaptations to the gas chromatograph and has the advantage of avoiding the need of any auxiliary thermal desorption and cryotrapping equipment.

Further possible applications of STs are the multi-channel thick film traps [53] and multi-channel open-tubular traps (MCT) [54] consisting of several STs filled into a thermodesorption glass tube. The usage of several tubes (3–8 tubes) provides a high silicone volume (typical volume: 635 μL) and offers very high analyte enrichment. The analytes are concentrated by purging the sample with a gas stream and collecting the stream on the MCTs [54]. In this application odour compounds from packaged long life milk were extracted and analysed with GC combination. In another application air containing several aromatic compounds was directly immersed onto the thick film silicone rubber traps followed by thermal desorption and GC analysis [53].

All the different described silicone extraction devices as well as further applications are summarized in Table 1.

### 4.2. SR/ST use in passive sampling devices

Passive sampling techniques allow the convenient determinations of the time weighted average (TWA) concentrations of freely dissolved contaminants over a certain period of time that is mostly weeks or months. The sampling devices are usually very small and simple in design, inexpensive and require no power supply. Calibration (i.e. determination of uptake rates for the target compounds) is a critical point in passive sampling and is usually performed in the laboratory. Most applied passive samplers are so-called permeation samplers, such as the semipermeable membrane device (SPMD) [55]. This sampler consists of a polyethylene tubing enclosing a thin film of triolein as collector phase. A main disadvantage of the SPMD is the intensive sample preparation work to recover the analytes from the triolein phase, which includes dialysis with considerable amounts of organic solvent, several solvent exchanges, and cleanup steps (e.g. preparative size-exclusion chromatography) before the chromatographic analysis. In the last years new passive samplers have been developed to overcome these problems and to make sample preparation easier and more applicable for routine monitoring. In this context passive samplers were developed that contain activated charcoal or a polymeric sorbent as collecting phase. Besides solid granular materials (such as Tenax, XAD, or Chromosorb) silicone materials are most applied polymers.

Vrana et al. [56] described the application of coarse pieces of silicone-based sorbent material as collecting phase of a passive sampler which is enclosed in a membrane bag during field exposure and can be retrieved loss-free for the following processing (in an analogous manner as described in Section 3.2). Different forms of the so-called MESCO device (that is the abbreviation for Membrane-Enclosed Sorptive Coating or Membrane-Enclosed Silicone Collector) have been developed meanwhile for time-weighted average (TWA) sampling of organic compounds in both water and air.

#### 4.2.1. MESCO for TWA sampling in aqueous environments

MESCOs used for water sampling can consist of different types of silicone collecting phases. Twister bars [56–58], ST [59,60], and SR [60–62] have been tested so far. In some MESCO applications cellulose membrane bags were applied around the collecting phase [56–58,62], whereas in others cellulose was replaced by low density polyethylene (LDPE) as it has proven to be more stable to biodegradation and solvents [60]. The advantage of using SRs and STs is the less fragility and low cost. On the other hand when working with water filled MESCOs for water sampling, water droplets can remain inside the STs disrupting GC–MS analysis. The MESCOs employing SRs as sampler and LDPE as membrane are the most promising configurations and current investigations deal with optimisation of the used membrane thickness and material [58].

#### 4.2.2. MESCO for TWA sampling in air

In parallel to the MESCO devices designed for passive sampling in water, two types of MESCOs for long-term monitoring of air pollutants were developed [63]. One type consists of an air-filled LDPE membrane (with different wall thicknesses) enclosing a Twister or a ST. Wennrich et al. [64] describe the application of MESCOs consisting of STs (volume of silicone: 250 μL), enclosed with a heat-sealed LDPE membrane tubing. They exposed the passive sampler for air sampling in a strongly polluted area for 28 days. After analyte enrichment, the STs were replaced from the membrane bag and directly thermodesorbed into the GC–MS system. A comparison between STs and stir bars as collection medium showed a very good performance of both samplers with the advantage of replacing the ST after one usage, avoiding cleaning and carry-over problems.

The second MESCO used for air sampling consists of a spiral-rod sampler, where a 158 mm long SR is mounted in a spiral flux on the top part of the sampler [65] providing a very high receiving surface (810 $mm^2$ instead of 167 $mm^2$ using a commercial stir bar). As transport-limiting and outer membrane LDPE is used which excludes also dust particles and water drops from the SR surface.

#### 4.2.3. Bare silicone material as passive sampler

Silicone material can also be applied without membrane protection for TWA sampling. We focus our report only on the use of small SR/ST pieces which can be processed in the solvent-free/-reduced manner as described above and will not discuss the use of silicone sheets, mats, etc. for field sampling which is usually connected with a large solvent consumption for back-extraction of the trapped analytes [66].

In a field study in Germany in summer 2003, 8 cm long SR pieces (2 mm diameter) alongside with SPMDs (as established sampler type) were exposed at six different points in the River Elbe and in the creek Spittelwasser for 22–28 days. Reasonable agreement of TWA concentrations estimated from the accumulated amounts of priority pollutants (selected PAHs and chlorinated hydrocarbons) based on laboratory-derived sampling rates was found [67]. The uptake rate of bare SR pieces are approximately ten times higher than those of the membrane-enclosed ones [61]. In 2005,

the performance of similar bare SR pieces (together with six other passive sampling devices) was evaluated through simultaneous exposures of 7–28 days in the River Meuse (The Netherlands) [62]. The TWA concentrations were calculated using exposure-specific sampling rates for the different types of samplers and target compounds. Therefore the samplers (i.e. the SR pieces) were spiked before deployment with so-called performance reference compounds (PRCs), typically deuterated or $^{13}$C-labelled analogies of several pollutants to be monitored. The measurement of PRC elimination provides information on exchange kinetics between water and the sampler (SR) and allows the estimation of sampling rates of contaminants in situ (see Ref. [62] for details). It was concluded that the most appropriate applications for samplers like the SR with low surface area and consequentially higher "field" LOD could be investigative monitoring tasks or monitoring at sensitive sites or where elevated concentrations are expected (e.g. sewage/storm water effluent).

At the same time Heltsley et al. demonstrated the use of small PDMS disks attached to fish as mobile passive sampler and compared the results with those from nonlethal fish tissue sampling and stationary passive sampling [68]. They also used the PRC approach to be able to adjust the sampling rates for the target analytes (PCBs and OCPs) empirically.

Pawliszyn et al. applied later comparable material, PDMS rods from Supelco (volume: 8 μL) for TWA sampling of PAHs in Lake Ontario [69,70]. Additionally, they took water samples from the sampling points and analysed them with direct SPME in the laboratory. They found a very good agreement for the higher concentrations (PAH concentrations of 50–80 ng/L) between passive sampling and direct SPME. For lower concentrations (13–20 ng/L) direct SPME was not sensitive enough attributed to the low sample and fibre volume. They concluded that silicone passive samplers have a strong potential for very sensitive, inexpensive and easy to use enrichment technique for the determination of TWA concentrations of pollutants in aqueous media. Also these authors used PRCs for the derivation of in situ (on-side) sampling rates and thus TWA concentrations, calling this on-rod standardisation technique. It was found by the authors that hydrodynamic conditions have considerably influence on the PAH amounts taken up by the PDMS rod [70].

All applications of passive samplers using SRs and STs are summarized in Table 2.

## 5. Conclusion and outlook

This review covers the developments and applications of SR and ST sorptive extraction. In their extraction mechanism they are very similar to SPME and, due to the similar applied silicone volume, to SBSE and can be seen as an alternative to these modern microextraction techniques. Main advantages of the SRs and STs are their low cost, robustness and high flexibility that allows addressing different demands of the extraction such as very small sample volumes. If stirring is preferred to shaking, magnetic steel wires or needles can easily be inserted into the materials as shown in Refs. [37,71]. About 20 publications in the field of SR and ST extraction are published so far and show the reliable applicability of these extraction materials. For an easy application and recognition of this extraction technique in future, a unified term is necessary. Silicone rod (SR) and silicone tube (ST) extraction seem to be suitable termini as they are applied in most of the existing publications.

Still several points have to be considered. The SRs and STs are not yet available in a commercial format and further detailed investigations on the material from different batches and suppliers are necessary. It has shown that the material is not as clean as pure PDMS that is applied for SBSE as higher background noise (silicones and alkanes from the material) are found using thermal desorption. It could help to have one supplier providing SRs and STs for sorptive extraction in analytical sample preparation. On the other hand this non-commerciality offers a large flexibility in terms of rod and tube dimensions (lengths, thicknesses). The STs and STs are easily available and easy to handle, they just have to be cut in pieces. After cutting the pieces are mostly weighted and only SRs and STs with deviations > 10% are employed.

Further potential of SR and ST extraction lies in their application for in situ derivatisation or post extraction derivatisation techniques. Different articles have shown the suitability of SBSE for in situ derivatisation of organic pollutants such as estradiol [72] and phenols [73]. In further studies SRs and STs could possibly be used in analogy to the Twister bars.

Another point that should shortly be addressed in the outlook is the increasing interest in analytical chemistry in direction of extracting polar analytes [74,75]. In SBSE, besides developing new materials suited for the extraction of volatiles (based partly on adsorption [76]), novel polymeric phases are employed. In this direction, Rodil et al. tested glass fibre fabric strips coated with a polyacrylate formulation as extraction medium [77]. Currently, a new Twister bar is commercialized by Gerstel with a polyacrylate coating providing promising properties towards extracting polar compounds [21]. Recently, the group of Nogueira developed and synthesized a stir bar consisting of polyurethane foams that showed high stability and good mechanical resistance to organic solvents. They tested the new stir bars for atrazine, 2,3,4,5-tetrachlorophenol, and fluorene [78], acidic pharmaceuticals [79] and triazines [80]. They found high effectiveness in the enrichment of polar compounds from water overcoming the limitations of the non-polar silicone phase.

Concerning SR and ST extraction, due to the easily availability and high flexibility of the material, a combination of tubes and rods with different materials (such as polyacrylate, polyurethane and polysulfone) to address different analyte polarities could be an interesting possibility which will be further investigated in the future.

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