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Stir Bar Sorptive Extraction (SBSE) applied to Environmental Aqueous Samples

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INTRODUCTION

For the analysis of organic compounds in aqueous environmental matrices several sample preparation methods are used. Volatile organic compounds can be analysed using (static) headspace, purge and trap or liquid-liquid extraction. Semivolatiles are analysed after liquid-liquid extraction or solid phase extraction (SPE).

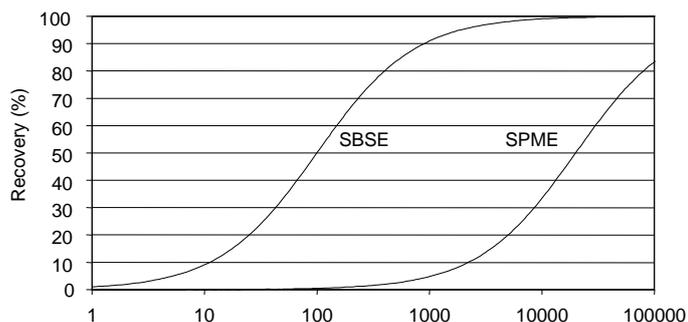
During the past years, miniaturisation has become a dominant trend in analytical chemistry. Typical examples of miniaturisation in sample preparation techniques are micro liquid-liquid extraction (in-vial extraction), ambient static headspace and disk cartridge SPE. In combination with state-of-the-art analytical instrumentation, this resulted in faster

analysis, higher sample throughput, lower solvent consumption, less manpower in sample preparation while maintaining or even improving sensitivity.

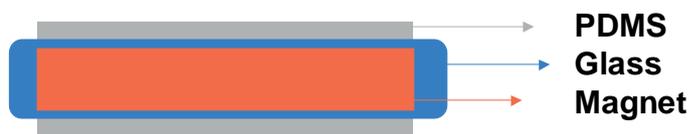
Some 10 years ago, a new micro-extraction method was developed by Arthur and Pawliszyn [1], namely solid-phase micro-extraction (SPME). SPME can be used for the extraction of organic compounds from aqueous samples or from a gas (headspace) phase. Mostly used are fibers coated with 7-100 μm polydimethylsiloxane (PDMS) as extraction medium. SPME is by nature an equilibrium technique, based on the partitioning of the solutes between the silicone phase and the aqueous (and/or gas) matrix. Recent studies [2-4] have correlated this equilibrium with octanol/water distribution coefficients ($k_{(o/w)}$). These studies demonstrated that for solutes with low $k_{(o/w)}$ ($k < 10000$) low recoveries are obtained. This is mainly due to the phase ratio between the aqueous and PDMS phase. The amount of PDMS used in SPME is typically in the order of 0.5 μL or less, thereby limiting the enrichment on the PDMS fiber.

Based on these observations, a new approach using **stir bars coated with PDMS** was recently developed [5]. In this approach, 50-300 μL PDMS coatings are used. Consequently, the sensitivity is increased by a factor of 100 to 1000. Complete recovery is possible for solutes with $k_{(o/w)}$ larger than 500. Solute with $k_{(o/w)}$ from 10 to 500 can also be analysed using calibration as is done in SPME. **This technique is called stir bar sorptive extraction (SBSE).**

A theoretical comparison between SPME and SBSE is given in the graph below showing the recovery (complete extraction of solutes into the PDMS phase) in function of the octanol - water distribution coefficient. While high recoveries ($> 50\%$) are only obtained for solutes with $k_{(o/w)} > 10000$ using SPME, the recovery obtained by stir bar sorptive extraction is already higher than 50 % for solutes with $k_{(o/w)} > 100$.



PDMS coated stir bars are now commercially available (Twister™, Gerstel GmbH). Magnetic stirring rods are incorporated in a glass jacket and coated with a 1 mm layer of PDMS. Two Twisters are available: 10 mm L x 3.2 mm o.d. and 40 mm L x 3.2 mm o.d. PDMS coated stir bars. Typically the 10 mm stir bars are used for 1-50 mL sample volumes and the 40 mm stir bars are used for 100-250 mL sample volumes.



EXPERIMENTAL

Sample preparation. Sample extraction is performed by placing a suitable sample amount (typically 10-25 mL) in a vial, adding a stir bar and stirring during 30-120 min. After extraction, the stir bar is introduced in a glass thermal desorption tube (4 mm i.d. x 187 mm L), placed in a thermal desorption unit and thermally desorbed. Desorption temperatures are application dependant and are between 150-300°C during 5-15 min. Alternatively liquid desorption can be used.

Instrumentation. For thermal desorption a TDS-2 system (Gerstel GmbH) is used. The thermal desorption unit is mounted on a HP 6890 GC (Agilent Technologies, Wilmington, DE, USA) equipped with a CIS 4 PTV inlet. The desorbed solutes are cryofocused in the PTV inlet. After desorption, the PTV is programmed to inject the solutes and analyse them on a capillary column.

RESULTS AND DISCUSSION

As predicted by theory, the absolute recovery obtained by stir bar sorptive extraction is higher than the recovery obtained by SPME. This is clearly illustrated by the analysis of a water sample spiked with polyaromatic hydrocarbons. For the SBSE experiment, a 60 mL water sample (5% methanol added to prevent wall adsorption) was spiked with 30 ng/L PAHs and extracted using a 10 mm stir bar. For SPME, a 60 mL sample spiked at 3000 ng/L was extracted using a 100 μm PDMS fiber. Extraction time was 30 min and stirring speed was 1400 rpm for both techniques. Desorption was done at respectively 250°C (SBSE)

and 300°C (SPME). The chromatograms are shown below.

With SBSE, all compounds are extracted to a similar extent, while in SPME the more apolar (higher boiling) solutes are extracted in higher amounts than the more polar (more volatile) PAHs.

The overall sensitivity using SBSE is also significantly higher (see Y-axis scale and the sample is 100 times more diluted for SBSE).

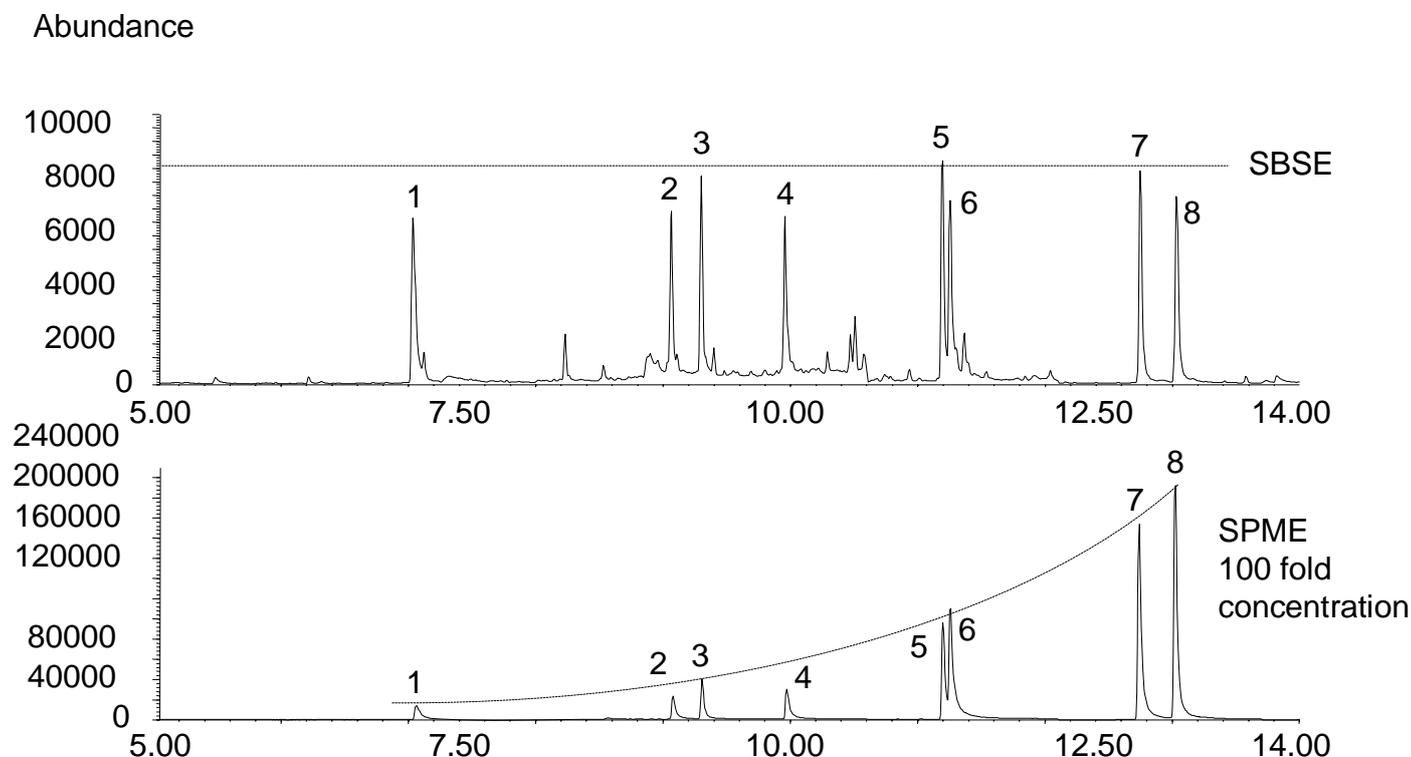


Figure 1. Comparison of relative recovery obtained for polycyclic aromatic compounds using SBSE versus SPME (Peaks: 1. Naphthalene, 2. Acenaphthylene, 3. Acenaphthene, 4. Fluorene, 5. Phenanthrene, 6. Anthracene, 7. Fluoranthene, 8. Pyrene).

Stir bar sorptive extraction can be used for both volatile and for semivolatile solutes. In this way, the same technique can cover EPA methods 524 and 624 (volatiles by GC-MS) AND methods 525 and 625 (semivolatiles by GC-MS). A typical analysis of a water sample spiked at 1 ppb level with a mixture of semivolatile priority pollutants is given in the chromatogram below. A 10 mL sample was extracted using a 10 mm stir bar during 40 min with stirring at 1400 rpm. The stir bar was then thermally desorbed at 250°C during 10 min in splitless mode. The desorbed solutes were cryofocussed in a CIS 4 PTV inlet at -50°C. After desorption the PTV was programmed to 300°C and the compounds were analysed on a 30 m x 0.25 mm i.d. x 0.25 µm HP-5 MS column. Detection was done using MS in scan mode. Compounds ranging from N-nitrosodimethylamine (peak 1) to chrysene (peak 35) are easily detected with LODs from 500 ng/L (for most polar nitrosamines) to 10 ng/L (for PAHs, phthalates, organochlorine pesticides, etc.).

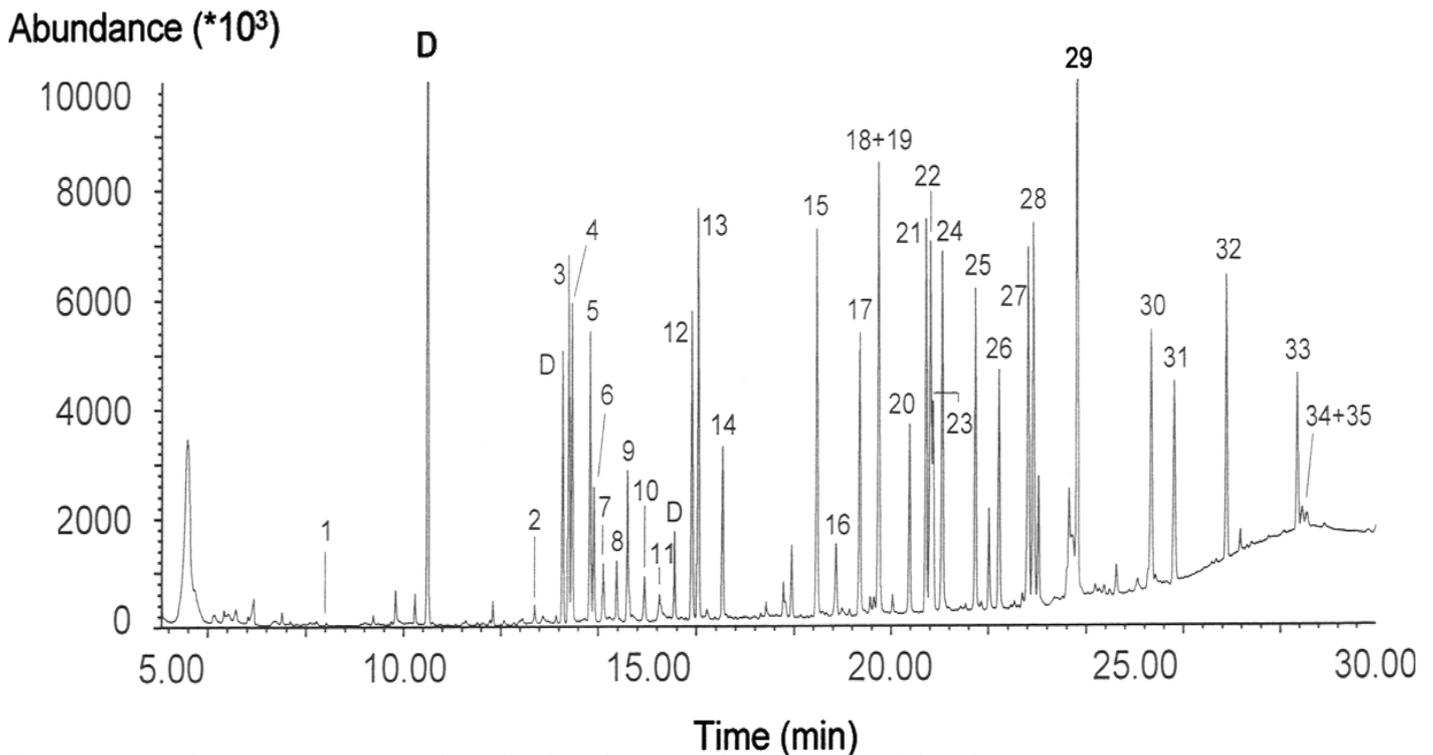


Figure 2. Analysis of water sample spiked with semivolatiles at 1 ppb level.

The analysis of volatiles by SBSE is given in the following chromatograms. A 10 mL sample was spiked at 2 ppb level and extracted using a 10 mm stir bar during 40 min with stirring at 1400 rpm. The stir bar was then thermally desorbed at 250°C during 10 min in splitless mode. The desorbed solutes were cryofocussed in a CIS 4 PTV inlet at -150°C. After desorption the PTV was programmed to 250°C and the compounds were analysed on a 30 m x 0.25 mm i.d. x 1 µm HP-1 column. Detection was done using MS in scan mode. Compounds ranging from 1,1,1-trichloroethane (peak 1) up to 1,2,3-trichlorobenzene (peak 44) are easily detected with LODs from 10-100 ng/L.

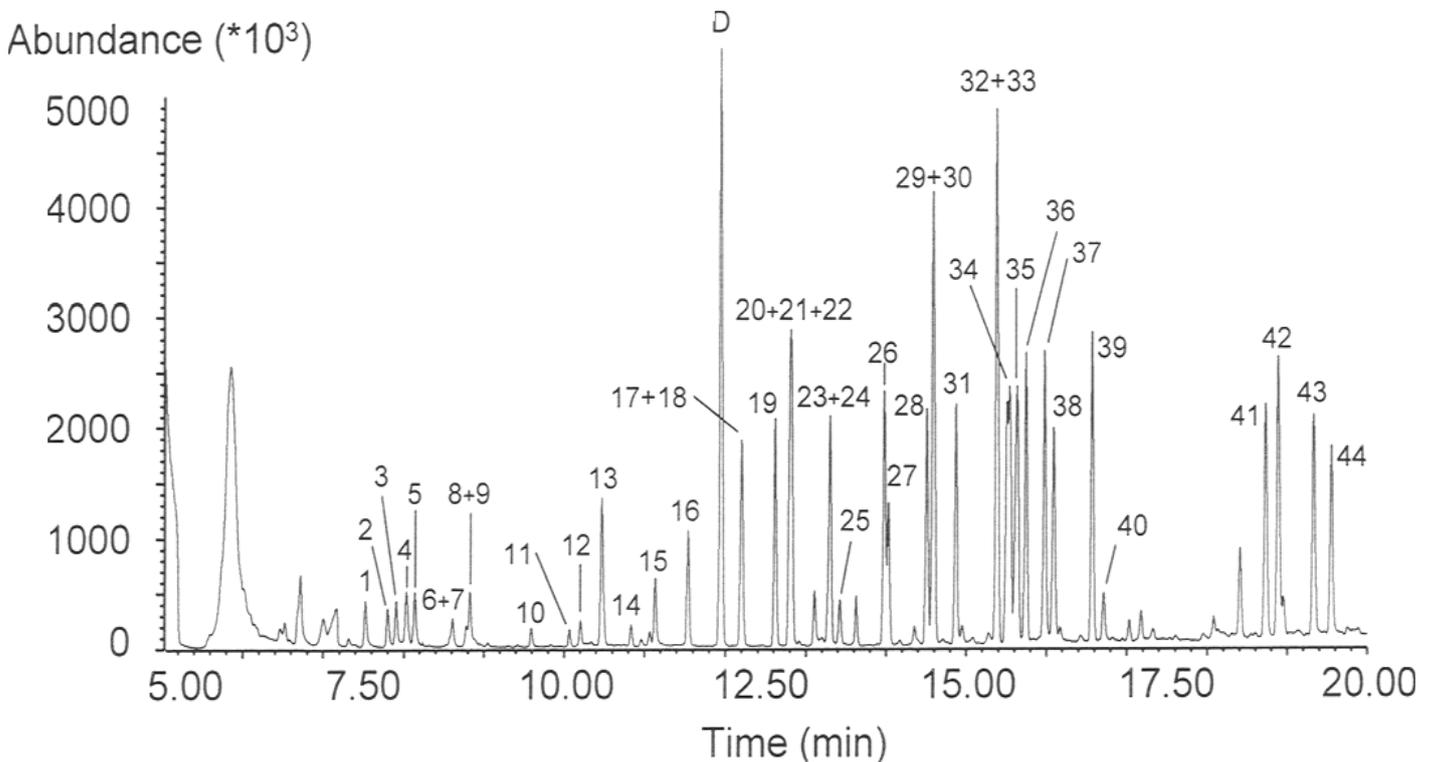


Figure 3. Analysis of water sample spiked with volatile priority pollutants at 2 ppb level using SBSE - thermal desorption - GC-MS.

The limits of the technique are illustrated by the analysis of a surface water sample. Stir bar sorptive extraction was done with a 40 mm stir bar in a 200 mL sample during 60 min at a stirring speed of 1000 rpm. The analysis was performed with the MS in scan mode. Volatile aromatic hydrocarbons are detected at 5 ppt level and dichlorobenzenes are detected at 1 ppt level.

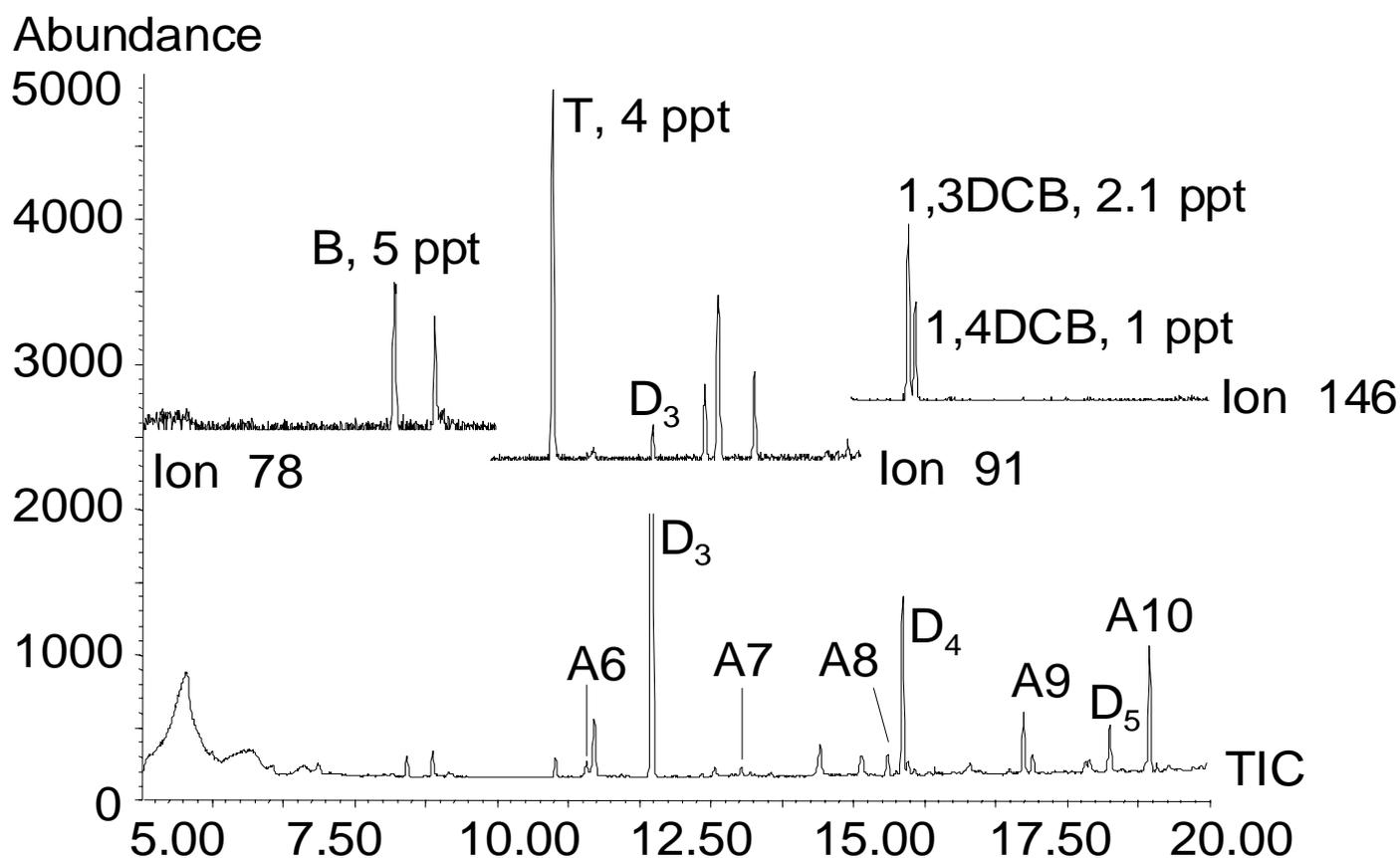


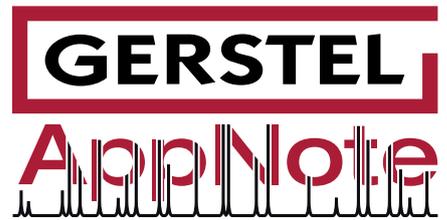
Figure 4. Analysis of surface sample by SBSE - thermal desorption - GC-MS (Peaks: B: benzene, T: toluene, 1,3-DCB: 1,3-dichlorobenzene, 1,4-DCB: 1,4-dichlorobenzene).

CONCLUSIONS

Stir bar sorptive extraction is a powerful technique for the extraction and analysis of both volatile and semi-volatile organic compounds in aqueous environmental samples. In comparison with SPME, higher recoveries and higher sensitivity are obtained.

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