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Comparison of the Sensitivity of Solid Phase MicroExtraction (SPME) and Stir Bar Sorptive Extraction (SBSE) for the Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Water and Soil Samples

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KEYWORDS

ABSTRACT

Two extraction techniques that avoid solvent consumption and cut down the sample preparation to a minimum - Solid Phase MicroExtraction (SPME) and Stir Bar Sorptive Extraction (SBSE) – were compared on the basis of their reproducibility and sensitivity for 16 US EPA PAH compounds.

Theoretical calculations indicated nearly quantitative recovery of all compounds under consideration except naphthalene for SBSE (10 mm GERSTEL TWISTER, $d_f = 0.5$ mm) whereas for SPME (100 µm PDMS) only higher boiling compounds benz[a]anthracene to benzo[g,h,i]perylene will show quantitative recovery and naphthalene for example will show only 10 % recovery.

For the comparison of both techniques, water samples spiked with 10 ppt to 4 ppb of PAHs and a NIST Standard Reference Material were used as model systems. For SBSE reproducibilities at 100 ppt (in water) were found to be in the range of 4 to 15 % for compounds from naphthalene to benzo[a]pyrene and between 18 and 28 % for indeno[1,2,3]pyrene, dibenz[a,h]anthracene and benzo[g,h,i]perylene. For SPME reproducibilities at 2 ppb were in the range of 7 to 15 % for compounds from naphthalene to pyrene and between 38 and up to 79 % for the higher boiling compounds. Both techniques showed good linearity for four-point calibrations. Detection limits were calculated to be in the range from 0.08 to 2 ppt for SBSE and 0.3 to 84 ppt for SPME.

The analysis of PAHs by SPME has certain limitations due to carry-over when using the 100 μm PDMS fiber. This problem is not encountered when using SBSE since we used multiple TWISTERs in parallel instead of using one TWISTER again and again. So far we did not test the behavior of TWISTER when running several samples one after another on the same stir bar.

First experiments with soil samples that contain a complex matrix indicated that both techniques can probably be used adequately for this analysis although the SPME technique showed too low sensitivity to quantitate the PAHs. This is most likely due to the fact that our very simple approach was insufficient to completely extract the PAHs from the soil into the liquid phase.

INTRODUCTION

PAHs are important priority pollutant organics. They emanate primarily from coal- and oil-burning plants and vehicle emissions as combustion products and are most likely adsorbed onto smoke particles settling on all kinds of surfaces, where they are transferred by rainfall into the aquatic environment. The analysis of waste and waste water is therefore mandated by most regulatory agencies like US EPA worldwide. Techniques applied for the analysis of PAHs are GC, GC/MS or HPLC. US EPA Methods 525, 610 and 625 describe the analysis of PAHs in drinking water, municipal and industrial waste water, US EPA Method 8100 in liquid and solid hazardous waste.

The analysis of water and soil for semi-volatile trace level contaminants entails the extraction of analytes from the matrix. This is usually performed by liquid-liquid (LLE) or solid phase extraction (SPE). In both cases analytes are extracted from the aqueous phase and dissolved into an organic solvent. This solvent is then evaporated to a small volume to concentrate the analytes and lower the detection limits. The evaporation of solvent can be eliminated when a PTV inlet is used and the large volume injection (LVI) technique is applied [1]. The process of extraction is on the one hand time consuming, tedious, and can lead to errors of contamination or spillage and on the other hand extractions require the use of organic solvents and often produce even more toxic waste. State-of-the-art procedures should be designed to minimize or completely avoid solvent consumption.

Arthur & Pawliszyn [2] developed a technique called SPME, where a fiber coated with an organic phase, such as polydimethyl-siloxane (PDMS) is used for sampling. The fiber is afterwards thermally desorbed to introduce compounds into the GC typically in the splitless mode. This approach has limitations including limited capacity of the fiber and potential contamination of the SPME needle assembly when sampling complex liquid matrices. Baltussen et al. [3] introduced a technique that uses a stir bar coated with PDMS material that is called SBSE. Due to the larger amount of PDMS relative to the SPME fiber this technique increases the recovery of analytes and therefore enhances the sensitivity.

THEORETICAL

The recovery of an analyte from a sample extracted by a sorptive process in equilibrium can be described from the following equation [3].

$$\frac{m_S}{m_0} = \frac{\left(\frac{K_{OW}}{\beta}\right)}{1 + \left(\frac{K_{OW}}{\beta}\right)}$$

m_S = amount of analyte in the PDMS
m_0 = total amount of analyte originally present in the water sample
K_{OW} = octanol-water partition coefficient
$\beta = V_w / V_S$ = phase ratio
V_w, V_S = volume of water and PDMS phase of the fiber/stir bar

Extraction with a phase like PDMS has the advantage that it is a pure sorptive process and no adsorptive

processes take place like with materials such as Carboxen/PDMS and Carbowax/Divinylbenzene. We used PDMS exclusively in this study for both SPME and SBSE.

The following table shows the experimental and/or predicted Log K_{OW} values and the calculated recoveries for the 16 EPA 610 PAH compounds under consideration in this work. The recoveries are calculated on the basis of a 10 mL sample volume, the 100 µm PDMS phase (0.612 µL PDMS) for SPME and the 10 mm TWISTER with a phase thickness of 0.5 mm (24 µL PDMS) for SBSE.

Table 1. Log K_{OW} values for US EPA 610 PAH as predicted from „SRC KowWin" ver 1.66 [4] and experimental values from references therein

Compound	CAS Number	Log K_{OW} (Exp./Calc.)	Recovery SPME	Recovery SBSE
Naphthalene	[91-20-3]	3.30 / 3.17	0.11	0.83
Acenaphthylene	[208-96-8]	3.94 / 3.94	0.35	0.95
Acenaphthene	[83-32-9]	3.92 / 4.15	0.34	0.95
Fluorene	[86-73-7]	4.18 / 4.02	0.48	0.97
Phenanthrene	[85-01-8]	4.46 / 4.35	0.64	0.99
Anthracene	[120-12-7]	4.45 / 4.35	0.63	0.99
Fluoranthene	[206-44-0]	5.16 / 4.93	0.90	1.00
Pyrene	[129-00-0]	4.88 / 4.93	0.82	0.99
Benz[a]anthracene	[56-55-3]	5.76 / 5.52	0.97	1.00
Chrysene	[218-01-9]	5.81 / 5.52	0.98	1.00
Benzo[b]fluoranthene	[205-99-2]	5.78 / 6.11	0.97	1.00
Benzo[k]fluoranthene	[207-08-9]	6.11 / 6.11	0.99	1.00
Benzo[a]pyrene	[50-32-8]	6.13 / 6.11	0.99	1.00
Indeno[1,2,3]pyrene	[193-39-5]	--- / 6.70	1.00	1.00
Dibenz[a,h]anthracene	[53-70-3]	6.80* / 6.70	1.00	1.00
Benzo[g,h,i]perylene	[191-24-2]	6.63 / 6.70	1.00	1.00

* Average from 3 references

From table 1 it is obvious that SBSE will theoretically lead to quantitative extractions for all compounds except naphthalene whereas SPME shows quantitative extractions only for compounds ranging from benz[a]anthracene to benzo[g,h,i]perylene. Using SPME, for example, the extraction efficiency for naphthalene will only be 10 %. For those compounds with quantitative recoveries there should be no advantage in using SBSE instead of SPME.

We evaluated this theoretical prediction by comparative measurements of PAHs in spiked water samples and soil samples.

EXPERIMENTAL

Instrumentation. All experiments were performed on a GC (6890, Agilent) with a mass selective detector (5973N, Agilent), a PTV inlet (CIS 4, Gerstel), an automated thermal desorption system (TDS 2/TDS A, Gerstel) and a MultiPurpose Sampler with SPME capability (MPS 2, Gerstel). All data were analyzed by using target ions in the extracted ion mode. As target ions we used the molecular ions for the PAH compounds under consideration.

SBSE was performed by GERSTEL TWISTER (10 mm; $d_f = 0.5$ mm) and for SPME we used 100 μm PDMS fiber assemblies.

Standards. For comparison of SPME and SBSE we either used MeOH/H2O spiked with a diluted 10 ppm EPA 610 standard in cyclohexane or MeOH/H2O extracts of a soil sample and a NIST SRM 1939 soil sample (PAH containing PCB reference material).

Analysis Conditions.

TDS (SBSE):	splitless
	20°C; 60°C/min; 300°C (10 min)
PTV (SBSE):	glass wool insert
	split 5:1
	-150°C; 12°C/s; 320°C (5 min)
PTV (SPME):	narrow bore insert
	split 5:1
	270°C
Column:	30 m HP-5MS (Agilent)
	$d_i = 0.25$ mm $\quad$ $d_f = 0.25$ μm
Pneumatics:	He, constant flow = 1.0 mL/min
Oven:	40°C; 10°C/min; 320°C (2 min)
MSD:	Scan; 35-400 amu

SBSE sampling.

Sample volume:	10 mL
Extraction:	ambient (60 min, 500 rpm)

SPME sampling.

Sample volume:	10 mL
Incubation:	35°C (10 min, 500 rpm)
Liq. extraction:	35°C (60 min, 250 rpm)

EXPERIMENTS

Dependence on MeOH concentration. For SPME and TWISTER we examined the influence of MeOH concentration on recovery of PAHs in aqueous solution. We compared results for 0 %, 10 % and 20 % MeOH concentration.

SPME fiber conditioning. Due to carry-over problems we evaluated the influence of a 5 min, 15 min and 25 min bakeout time in the inlet.

SPME agitator temperature. PAH samples were analyzed at 80 °C and 35 °C agitator temperature.

SPME inlet flow. To evaluate the desorption efficiency of PAHs from the PDMS fiber we compared splitless and 10:1 split desorptions. The precision and sensitivity experiments were performed using a 5:1 split for the desorption.

Reproducibility experiment. 15 replicates of a 100 ppt (SBSE) or 2 ppb standard (SPME) were analyzed.

Sensitivity experiment. In addition to the 15 replicates we analyzed 5 samples of 3 different concentrations; SPME: 1, 3 and 4 ppb; SBSE: 10, 40 and 80 ppt.

Soil experiments. 1g of NIST SRM 1939 was slurried in 20 mL H2O (10 % MeOH) and placed in an ultrasonic bath for 10 min. 1 mL of this extract was diluted to 11 mL H2O with 10 % MeOH after settling of the sediment. 10 replicates were extracted and analyzed by TWISTER and SPME.

RESULTS AND DISCUSSION

Dependence on MeOH concentration. Several authors indicate that PAH compounds are lost to glass walls, if water is the only solvent used. MeOH or Hyamine, an ionic tenside, are added to the samples to keep PAHs in solution [5, 6]. We performed a rough experiment with water spiked with 10 ppb EPA 610 PAHs (TWISTER) and 4 ppb (SPME). Experiments for SBSE indicated that the addition of MeOH increases the recovery of PAHs in water but concentration (10 % or 20 % MeOH) made no significant difference. Our first experiments during SPME method development led to very poor precision. To exclude that the 10 % MeOH led to competition with PAHs on the fiber we performed one series with water as the only solvent. This series showed even worse precision probably due to the loss of PAHs on glass walls. The addition of organic solvents to the water will change the activity coefficients of the analytes in water, and thus could affect the partitioning of the compounds into the PDMS phase. The simple

formula describing the partitioning between water and PDMS is therefore no longer valid and recoveries will be different than calculated. To avoid the change in activity coefficients by the addition of organic solvents silanized vials can be used instead to keep the compounds in solution [7]. Further studies would be necessary to clarify the influence of MeOH concentration on SPME recovery of PAHs and determine the influence of the PAH concentration or using silanized vials. For all subsequent experiments we decided to continue with 10 % MeOH added to the samples.

SPME fiber conditioning. Due to carry-over we found very poor precision for SPME when working with desorption/bakeout times of 5 minutes and splitless desorption. We therefore increased the bakeout time in the inlet to 25 min while the split is set to 50:1 after 3 min splitless operation. This only improved the precision for the lower boiling PAHs.

SPME agitator temperature. Although a compound-specific positive influence of temperature on recovery of PAHs is described by Thurow & Koch [8] for SBSE, our SPME experiments indicated that the recovery increased 2- to 5-fold when changing the agitator temperature from 80 °C to 35 °C. For SBSE no experiments regarding a temperature influence were conducted.

SPME inlet flow. Because of the poor precision for SPME during method development, we decided to evaluate the efficiency of desorption of PAHs from the PDMS fiber by comparing splitless and 10:1 split desorptions of the fiber using a 4 ppb PAH standard. We were wondering if a higher flow through the PTV inlet would improve the reproducibilities although we were already using a special liner with an ID of only 0.8 mm. On the other hand sometimes liners with larger inner diameters like 2 mm are recommended for liquid SPME applications [7]. That is due to the fact that water may be trapped between the SPME fiber rod and the protective sleeve by capillary forces. This water will evaporate rapidly inside the liner at the high temperature used to desorb the compounds from the SPME fiber and will lead to overloading of the narrow-bore liner. In that case compounds will be lost through the septum purge line of the inlet. To evaluate the desorption efficiency we plotted the ratio of the peak area of the split measurements (x 10) and splitless measurements expecting a ratio of 1. Figure 1 shows the result of the comparison.
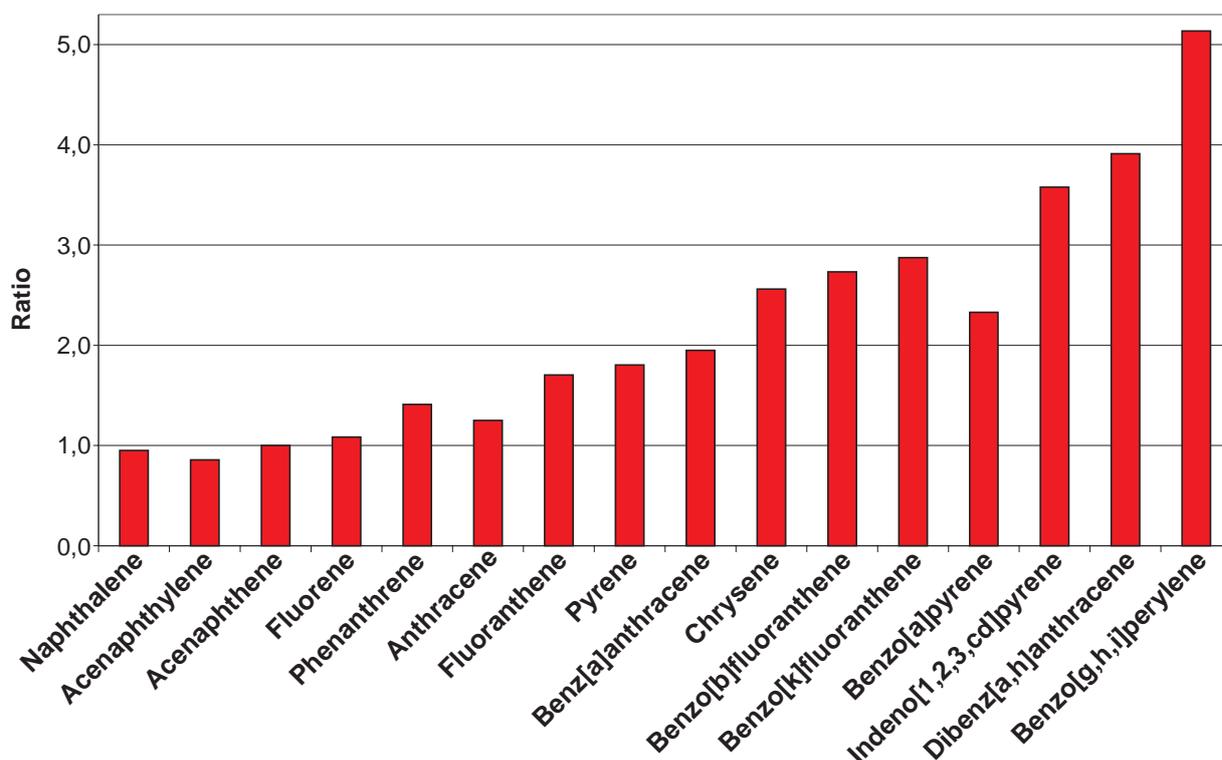

Figure 1. Ratio of peak area of 10:1 split (x 10) injection to splitless injection.

As shown in Figure 1 values around 1 (0.86 to 1.25) were found for compounds ranging from naphthalene to anthracene but much higher values than that for the higher boiling compounds (up to 5 for benzo[g,h,i]perylene). This clearly indicates that splitless desorption of PAHs from the 100 µm PDMS fiber is not complete. We do not find any indication that a liner with a larger inner diameter would improve our results. If the evaporation of water from the fiber and loss of compounds through the septum purge line would be the problem, we would expect that especially lower boiling compounds are lost but values around 1 are found for the lower boiling PAHs. We therefore decided to compromise between quantitative desorption and limited sensitivity by using a split ratio of 5:1 and 15 min fiber bakeout for the following experiments.

Reproducibility experiment. Our experiments were designed to compare SPME and SBSE on the basis of their repeatability in typical laboratory use. We did not evaluate SPME fiber to fiber reproducibility since we performed our measurements using an automated sampler. For SBSE on the other hand it is typical to extract several samples at a time to save over all analysis time. The different approach for both techniques of course has advantages and disadvantages. For SBSE problems due to carry-over on the TWISTER can now be neglected, but TWISTER to TWISTER reproducibility is taken into account. For SPME on the other hand carry-over has to be considered but fiber to fiber reproducibility is not evaluated. SBSE experiments performed by Thurow & Koch [8] indicated that carry-over cannot be neglected for all PAHs under consideration. We evaluated SBSE carry-over by desorbing the same TWISTER twice. When reusing the TWISTER without reconditioning we found carry-over up to 15 % (Naphthalene). This problem might disappear by increasing the TDS final time. For SPME, carry-over, especially for the four-ring systems and higher, is also a major concern and in the literature very high desorption temperatures are recommended [9]. This is of course limited by the upper temperature limit of the fiber (280 °C for 100 µm PDMS). In terms of carry-over it might be worth considering the 7 µm or 30 µm PDMS fiber but this will likely lead to lower sensitivities, i.e. higher detection limits. Probably the 30 µm PDMS fiber is the better choice since the 7 µm fiber is different regarding the linkage of the PDMS material and will behave differently [10].

The precision results obtained for both SPME and SBSE are shown in table 2.

Table 2. Precision from 15 measurements at 100 ppt (SBSE) and 2 ppb (SPME).

Compound	Precision SBSE [%]	Precision SPME [%] *
Naphthalene	4.3	14.7
Acenaphthylene	9.2	9.6
Acenaphthene	7.7	9.3
Fluorene	8.4	7.7
Phenanthrene	8.5	9.9
Anthracene	7.9	12.5
Fluoranthene	7.2	14.4
Pyrene	6.7	13.6
Benz[a]anthracene	10.5	41.9
Chrysene	8.7	37.8
Benzo[b]fluoranthene	14.7	51.7
Benzo[k]fluoranthene	7.6	49.7
Benzo[a]pyrene	13.3	54.3
Indeno[1,2,3]pyrene	25.6	79.2
Dibenz[a,h]anthracene	28.1	73.9
Benzo[g,h,i]perylene	18.6	58.0

* Literature data describe reproducibilies for SPME of less than 12 % for all compounds [9]. The data in the table is the best we obtained with the limited SPME optimization we performed.

Table 2 shows precision results for the 16 EPA PAHs that are very different for both techniques. For SPME we found reproducibilies typical compared to the literature [8, 9] only for compounds ranging from naphthalene to pyrene. Our SPME data for the PAH concentration of 3 ppb showed slightly better precision for the higher boiling PAHs (17 to 47 %). The very poor precision found for the higher boiling PAHs is probably due to insufficient desorption from the PDMS fiber. We believe that the 2 step desorption process of SBSE is beneficial for the analysis of high molecular

compounds like PAHs. The use of the CIS as a cryo trap in the venting mode allows high desorption flows without the need to split the sample. For SPME a split seems to be necessary to efficiently desorb the PAHs from the 100 μm PDMS fiber. Although further method development is expected to improve the precision, we believe that both techniques would show improvement.

For SBSE long term storage of the TWISTERs in the TDS A might be a problem. Haesselbarth [11] indicated that losses of sorbed compounds (5 to 40 %) can be observed when the residence time of TWISTERs in the TDS A autosampler exceeds 20 hrs. This effect may of course influence the precision when working with long sequences but probably only for compounds more volatile than PAHs.
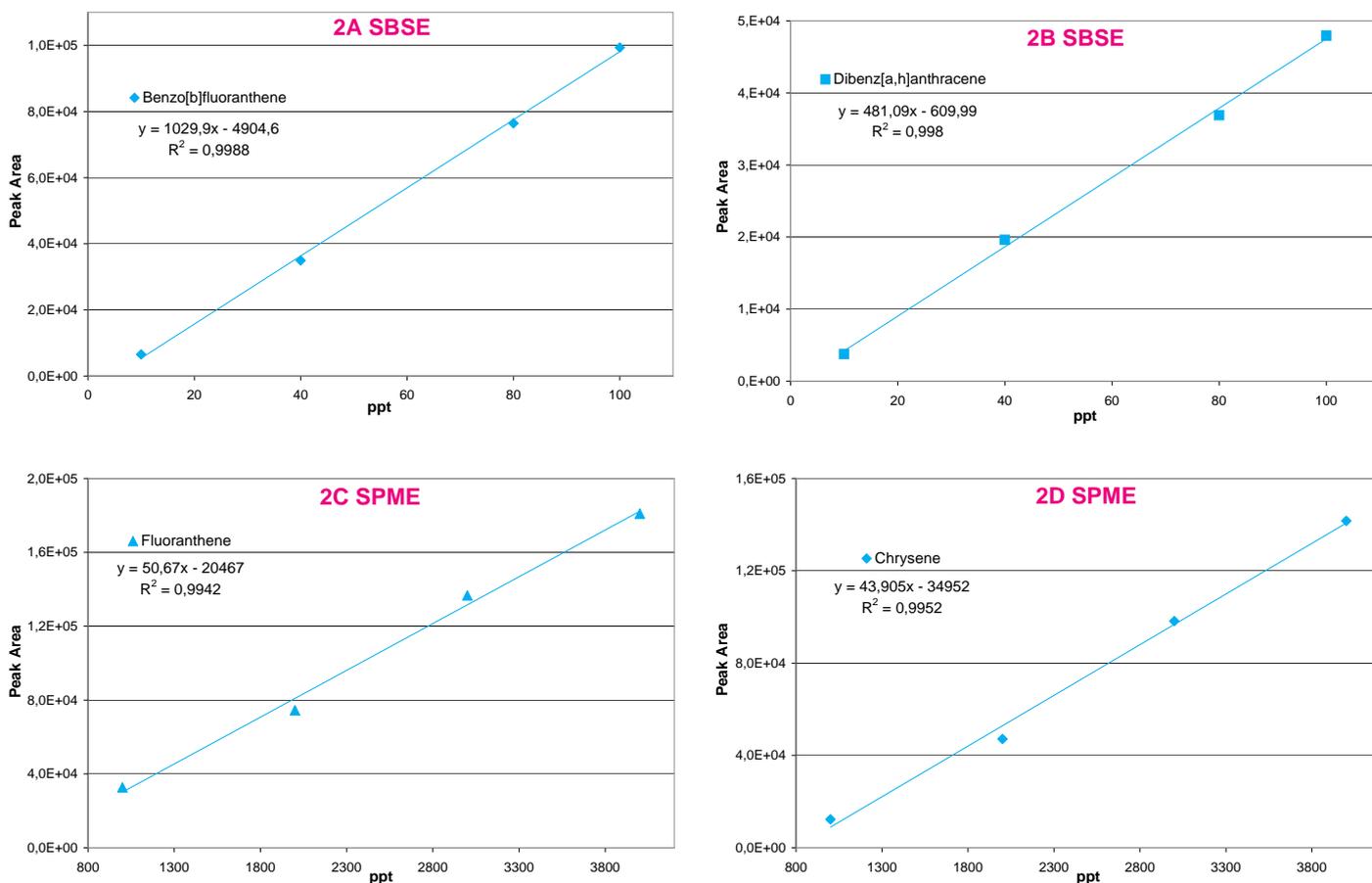
Sensitivity experiment. We performed four-point calibrations for both techniques. Due to limited sensitivity of the SPME techniques we had to use 100 times higher concentrations than for SBSE. Calibrations for SBSE were performed at 10, 40, 80, and 100 ppt, while 1, 2, 3, and 4 ppb were used for SPME. Table 3 shows sensitivities, linearities, and detection limits obtained for SBSE and SPME.

Table 3. Sensitivities, linearities, and detection limits as calculated from four different concentrations per extraction technique (SBSE: 10, 40, 80, 100 ppt; SPME: 1, 2, 3, 4 ppb)

Compound	SBSE			SPME		
	Sensitivity [area/ppt]	Det.Limit [ppt]	Linearity	Sensitivity [area/ppt]	Det.Limit [ppt]	Linearity
1 Naphthalene	638	0.5	0.9877	9	83.8	0.9511*
2 Acenaphthylene	699	0.1	0.9457	9	16.5	0.9781
3 Acenaphthene	466	0.6	0.9407	18	5.1	0.9653*
4 Fluorene	562	0.1	0.9651	21	11.6	0.9725*
5 Phenanthrene	792	0.9	0.9832	34	4.2	0.9842
6 Anthracene	836	0.2	0.9780	31	1.1	0.9907
7 Fluoranthene	1091	0.7	0.9976	51	1.7	0.9942
8 Pyrene	1122	1.3	0.9976	55	3.6	0.9946
9 Benz[a]anthracene	1026	1.2	0.9948	32	0.3	0.9726
10 Chrysene	1031	1.8	0.9954	44	1.4	0.9952
11 Benzo[b]fluoranthene	1030	0.5	0.9988	40	2.3	0.9768
12 Benzo[k]fluoranthene	1123	0.1	0.9947	43	5.1	0.9850
13 Benzo[a]pyrene	931	0.5	0.9973	28	6.0	0.9697
14 Indeno[1,2,3]pyrene	538	0.2	0.9886	23	7.0	0.9603
15 Dibenz[a,h]anthracene	481	0.3	0.9980	16	2.6	0.9065
16 Benzo[g,h,i]perylene	577	0.2	0.9794	26	6.3	0.9133

* = regression uses 3 data points (1, 2, and 3 ppb) only.

The sensitivities in table 3 show 20 to 80 times higher sensitivities for SBSE than for SPME. The regression coefficients (r^2) show good linearities for both SPME and SBSE in the concentration ranges under consideration. For naphthalene, acenaphthene and fluorene the calibration curves indicated that the 4 ppb sample is above the linear range of the SPME method. We therefore neglected these data points for the linearities of these three compounds. Further studies would be necessary to determine the linear range of the method. Figures 2A to 2D show four diagrams of area counts versus concentration and the regression lines.

2A SBSE

◆ Benzo[b]fluoranthene

$y = 1029,9x - 4904,6$
$R^2 = 0,9988$

2B SBSE

■ Dibenz[a,h]anthracene

$y = 481,09x - 609,99$
$R^2 = 0,998$

2C SPME

▲ Fluoranthene

$y = 50,67x - 20467$
$R^2 = 0,9942$

2D SPME

◆ Chrysene

$y = 43,905x - 34952$
$R^2 = 0,9952$

Figures 2A to D. Plots of area counts versus concentration and parameters of the linear regression for benzo[b]fluoranthene and dibenzo[a,h]anthracene for SBSE and fluoranthene and chrysene for SPME.

The detection limits in table 3 are theoretical statistical values based on the fluctuations of the baseline and the sensitivity of the method (slope of the calibration curve). The calculated detection limits for SPME are comparable to data cited in the literature. Pawliszyn [9] and references therein state detection limits for PAHs by SPME in the range from 0.001 to 0.42 ppb. Theoretically SBSE is in most cases more sensitive (up to 200 times) than SPME.

When looking at the measurements it becomes obvious that SBSE is indeed far more sensitive than SPME (Fig. 3).
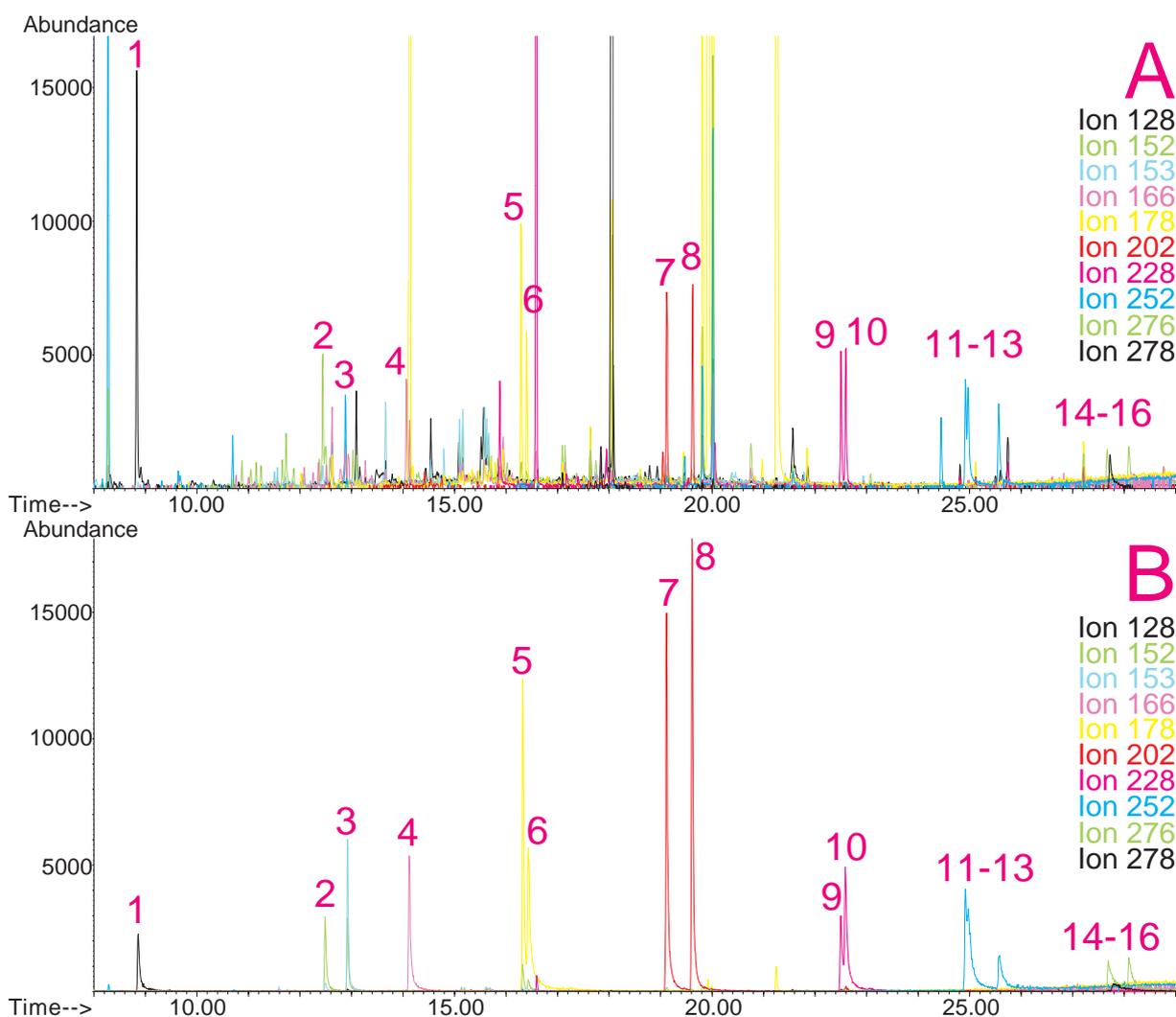
Figure 3. Overlay of extracted ion chromatograms (m/z : 128, 152, 153, 166, 178, 202, 228, 252, 276, 278) for SBSE (10 ppt, upper trace) and SPME (1 ppb, lower trace), peak identities see table 3.

Note that similar peak heights are obtained for several compounds although the PAH concentration used for SBSE is 100 times lower than that used for SPME. The background signal is of course also increased for SBSE compared to SPME. From peak areas obtained for SPME at 1 ppb the effective limit for peak detection can be estimated to be at 300 to 600 ppt depending on the compound. For SBSE on the other hand the effective limits for peak detection can be estimated to be in the range of less than 1 to 4 ppt. For practical purposes the limit for peak detection found for SBSE is about a factor of 100 lower than that found for SPME. This is not consistent with the about 40 times higher phase volume for SBSE. From the theoretical prediction of recoveries one should expect that there is no difference in sensitivities and detection limits for all compounds with predicted recoveries of 1. The inconsistency from the theoretical prediction may have several reasons:

1) The formula for the theoretical prediction is no longer valid since we added 10 % of an organic solvent to the standards which changes the activity coefficients for the partitioning of compounds into the PDMS.
2) The effective volume of the PDMS material which is linked to the SPME fiber may be different than from theoretical calculations.
3) There may be displacement effects happening especially on the SPME fiber since there is less PDMS material available.
4) The SPME extraction of compounds from the aqueous phase may be not quantitative due to the slow agitation instead of fast stirring which is recommended in the literature despite the 60 minute extraction time.
5) Since we found that carry-over plays a role for SPME we might not have transferred the extracted compounds quantitatively onto the GC column.

From our data we cannot decide what the reason for the inconsistency from the theoretical predictions is and it may well be a combination of several reasons although some points from the list clearly have a tendency to have a higher effect than others. Irregardless of the mechanism, recovery with the SPME technique seems to be not behaving as predicted for the recoveries. That points out that it may well be worth trying SBSE instead of SPME even though no improvement is predicted from theoretical considerations.

Soil experiment. To study the effect of a complex solid matrix on reproducibility of PAHs we used a NIST SRM 1939 soil sample. After liquid extraction in an ultrasonic bath we took 10 aliquots each of the liquid and extracted this by SBSE and SPME after dilution. The SRM 1939 material is known to contain phenanthrene (130 ppb), fluoranthene (190 ppb), pyrene (170 ppb), benz[a]antharacene (46 ppb) and chrysene (51 ppb). Given a theoretical quantitative extraction of the soil sample by our simple sample preparation approach, we diluted the PAHs to concentrations between 209 and 864 ppt. When analyzing by SBSE we found reproducibilities ranging from 12 to 20 % for the 10 replicates. Unfortunately the sensitivity of SPME was not high enough to analyze the samples. This was expected since the concentrations after dilution are in the ppt range and in addition our extraction approach cannot be expected to be quantitative. Given a theoretical quantitative extraction of PAHs by the TWISTER we can estimate the extraction efficiency of our simple approach to be in the range of only 2 to 5 %. Figure 4 shows an overlay of the extracted ion chromatograms for the soil sample for SBSE and SPME.
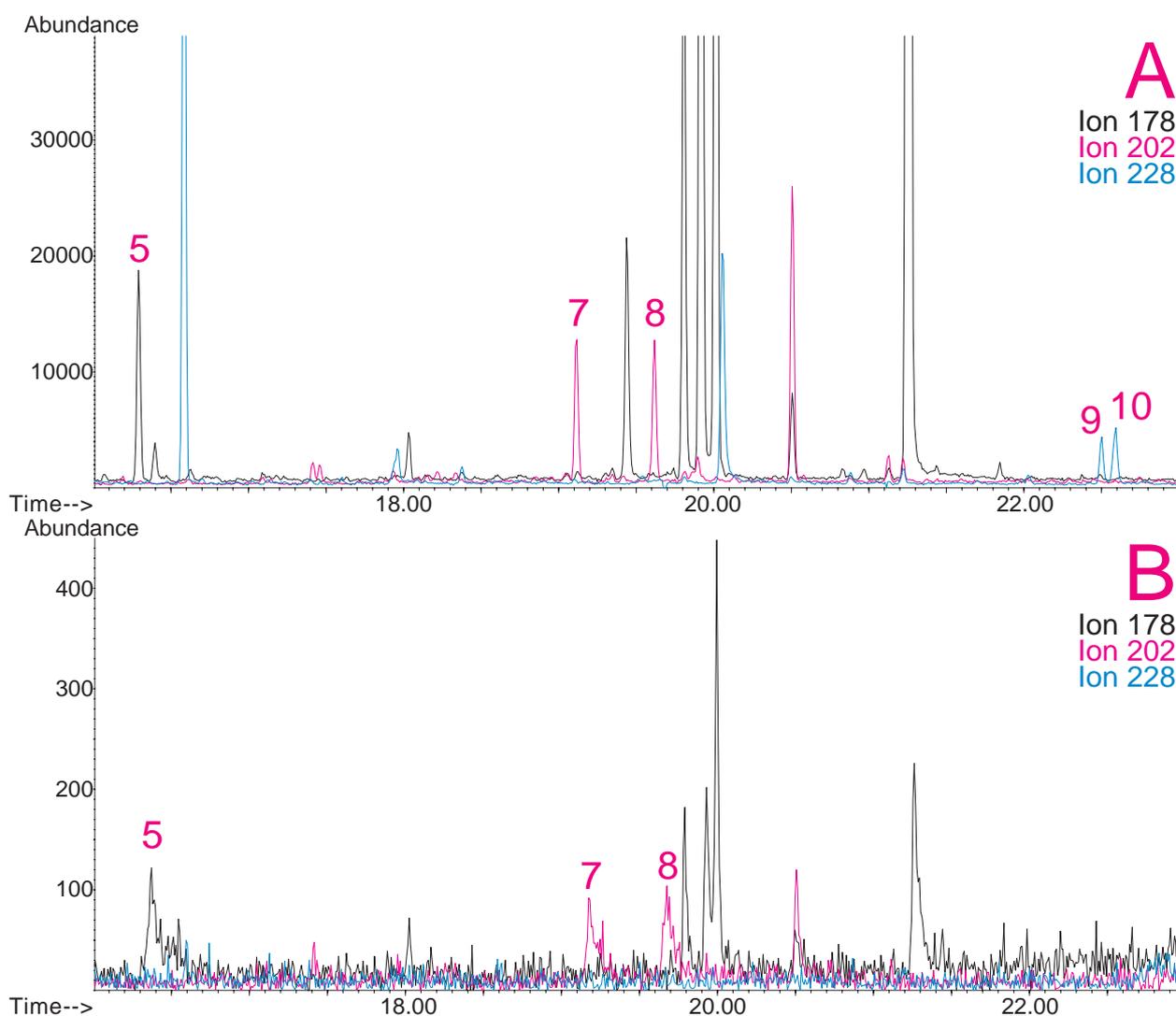

Figure 4. Overlay of extracted ion chromatograms (m/z = 178, 202, 228) of the NIST SRM 1939 soil sample for SBSE (A) and SPME (B) showing PAHs.

Extractions of soil are mainly done using organic solvents like methylene chloride since water extracts cannot be used with the subsequent GC analysis. Using the SBSE technology extractions using water are possible since the TWISTER can recover the dissolved compounds from such an extract and subsequent thermal desorption of the TWISTER allows sample introduction without water into the GC system. First experiments using Accelerated Solvent Extraction (ASE) of soil samples with water and a small percentage of a polar organic solvent like 10 % of methanol, acetonitrile or propanol and subsequent extractions by TWISTER led to promising results [12].

Besides the PAH compounds the SRM material has certified contents of several PCBs. These and other PCBs can be found in the chromatogram of the SRM extract (Fig. 5) but were not evaluated in this study.
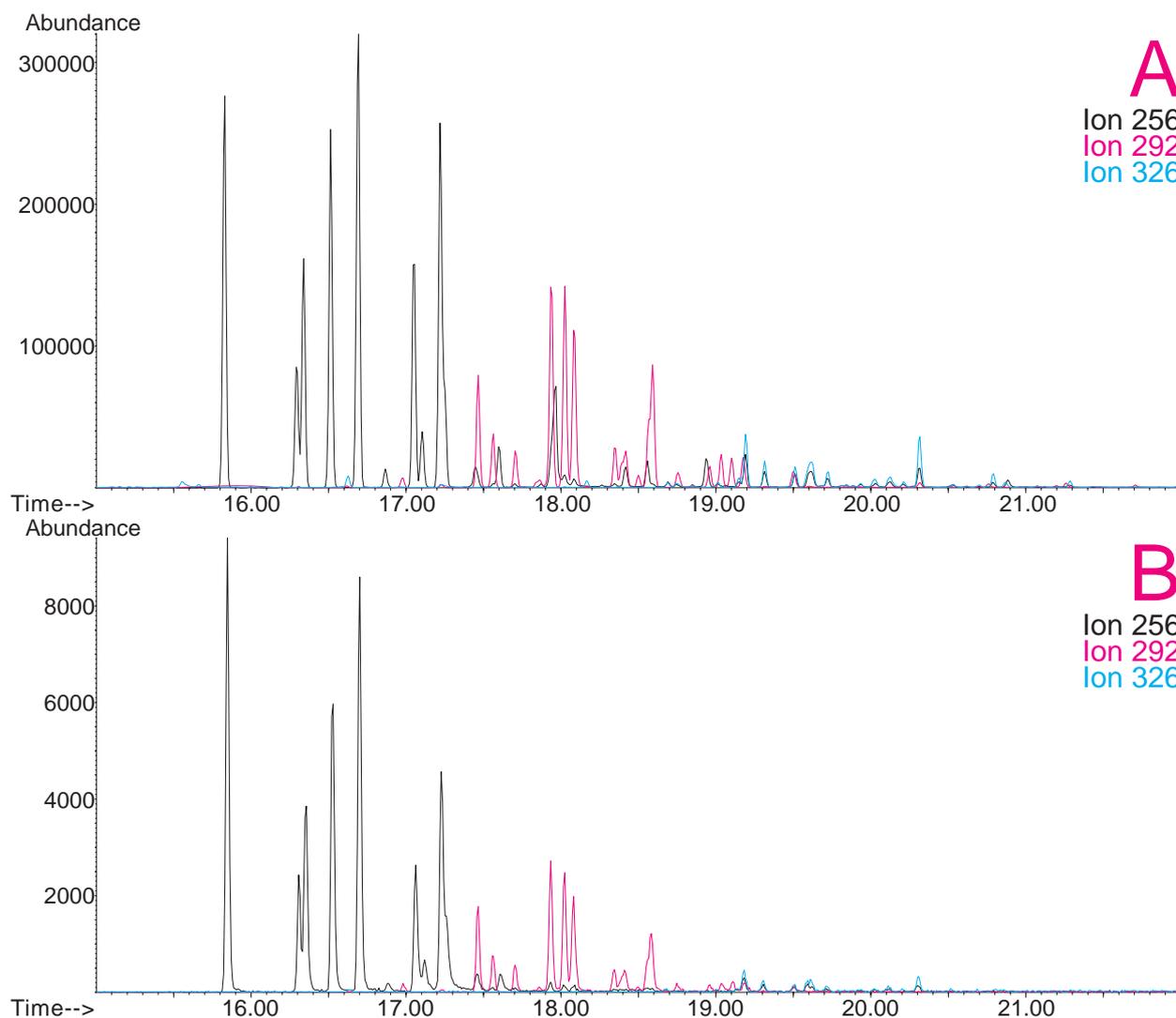

Figure 5. Overlay of extracted ion chromatograms (m/z = 256, 292, 326) of the NIST SRM 1939 soil sample for SBSE (A) and SPME (B) showing PCBs (Trichlorobiphenyls: c = 2.2 – 6.9 µg/g; Tetrachlorobiphenyls: c = 0.9 – 4.5 µg/g; Pentachlorobiphenyls: c = 0.5 – 0.8 µg/g).

Figure 5 shows that SBSE is again leading to a much higher response compared to SPME chromatogram for the same sample.

CONCLUSIONS

Method optimization for both techniques – SPME and SBSE – is challenging since several parameters play a role in the analysis of PAHs. We found that the concentration of MeOH, the temperature of the agitator during sampling and the desorption flow are critical to the measurements.

For SBSE the problem of desorption does not play as important a role as for SPME since the desorption is performed in two steps using the PTV in the cool venting mode. The PAHs can be desorbed from the PDMS using a high flow while the compounds are refocussed on the CIS liner.

Although more optimization of the analytical methods (salt saturation, fast stirred samples, a neutral pH [9] and different liner diameter or silanized vials [7]) are necessary, we do believe that this difference in sensitivity will remain, since the difference is largely due to the difference in PDMS phase volume between SBSE and SPME.

The problems with precision found for SPME analysis indicate that desorption of PAHs from the 100 μm PDMS fiber is a problem. Precision may improve when using a 30 μm or even 7 μm PDMS fiber.

Our data indicate that SBSE is about a factor of 20 to 80 more sensitive for the analysis of PAHs from aqueous samples than SPME. The theoretical detection limits calculated for SBSE are in most cases lower (up to 200 times) than for SPME. As far as we can tell the SPME technique seems to be not behaving as predicted for the recoveries, because otherwise no improvement in sensitivities and detection limits for the higher boiling PAHs would be possible. Further decrease of detection limits may be considered to be possible by using either the TWISTER with 1 mm film thickness or the 20 mm TWISTER instead of the standard 10 mm bar.

Even a strong matrix like a PAH containing sediment allows the analysis of PAHs after effective extraction from the soil.

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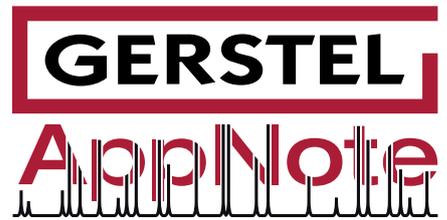
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