

Figure 7 Average percent relative recovery data of 56 semi-volatile base/neutral/acid components extracted from three soil types using PFE. Soils were fortified at 250, 2500, and 12500 $\mu\text{g kg}^{-1}$. (Data from Richter *et al.* (1995) reproduced with permission from International Scientific Communications Inc.)

will continue to use PFE to develop many more environmental sample applications.

See also: **II/Extraction:** Supercritical Fluid Extraction. **III/Environmental Applications:** Supercritical Fluid Extraction; Soxhlet Extraction. **Superheated Water Mobile Phases:** Liquid Chromatography.

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Solid-Phase Microextraction

T. Nilsson, Technical University of Denmark, Lyngby, Denmark

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Solid-phase microextraction (SPME) is a technique for the extraction of organic compounds from gaseous, aqueous and solid matrices such as many environmental samples. It is rapid and simple, which makes it ideal for automation and *in situ* measurements, and no harmful solvents are used. The principle of SPME is equilibration of the analytes between an organic polymeric phase coated on to a fused-silica fibre and the sample matrix. The parameters of importance for the equilibration process are described below and

various environmental applications are discussed. Traditionally, SPME has been combined with analysis by gas chromatography (GC), and mainly aqueous samples have been analysed. This combination has proved to be sensitive, accurate and precise for the quantitative analysis of volatile organic compounds and different classes of pesticides. Solid samples can also be analysed by SPME in spite of the stronger matrix effects, and recently SPME has been coupled with liquid chromatography (LC) for the analysis of polar pesticides.

Principle

The principle of SPME is that a fused-silica fibre is coated with an organic polymer and exposed to the

sample. The fibre is mounted inside a steel syringe needle for protection in order to be able to penetrate the septum of the sample vial and the GC injector without damaging the fibre. Subsequently, the fibre can be pushed out of the needle for exposure to the sample. The analytes will then diffuse into the fibre coating until equilibrium has been established.

Extraction Efficiency

Basically, the extraction efficiency is determined by the extraction time, the sample concentration and the distribution constant of the analyte between the fibre coating and the sample. The classical situation is extraction with the fibre immersed in a water sample.

The amount of analyte extracted by the fibre coating equilibrium n_1^∞ is determined by the expression:

$$n_1^\infty = \frac{KV_1V_2C_2^0}{KV_1 + V_2} \quad [1]$$

where K is the distribution constant, V_1 is the volume of the fibre coating, V_2 is the sample volume, and C_2^0 is the initial sample concentration.

Another SPME approach is sampling from a headspace above the sample in the vial. In this case, the amount of analyte adsorbed after infinite time n_1^∞ is given by the equation:

$$n_1^\infty = \frac{C_2^0V_1V_2k}{kV_1 + k'V_3 + V_2} \quad [2]$$

where V_3 is the volume of the headspace, k is the fibre coating–gas distribution constant, and k' is the gas–water distribution constant of the analyte. k' is directly proportional to Henry's constant and is usually relatively low for the compounds analysed by SPME. Thus, only if V_3 is considerable compared to V_2 , a lower sensitivity will be observed with headspace–SPME (HS–SPME). The advantage of HS–SPME is that equilibration times will be much shorter due to the fact that the diffusion is several orders of magnitude faster in the gas phase than in liquids. Another advantage of HS–SPME is that it can be applied for the analysis of solid and dirty samples. However, such applications are not so amenable to

a theoretical treatment because of unpredictable matrix effects.

Adsorption Kinetics

Basically, the kinetics of adsorption are governed by diffusion. A number of models have been reported for different situations, but they provide only approximate descriptions under ideal conditions. In practice, a number of factors will cause deviations from these conditions, thus a simple, empirical model has been described for practical purposes:

$$n_1 = n_1^\infty [1 - \exp(-t/\tau)] \quad [3]$$

where τ is a measure of the equilibration velocity, and n_1 is the amount adsorbed on the fibre coating at the time t .

Extraction

The extraction conditions are optimized in order to obtain a rapid and sensitive analysis. It is important to remember that SPME depends on diffusion and distribution. Thus, the required extraction time can be reduced by increasing the diffusion rates, and the extraction efficiency can be improved by increasing the distribution constant.

Choice of Fibre Coating

Various SPME fibres are commercially available (Table 1). The polydimethylsiloxane (PDMS) coating is recommended for the extraction of nonpolar compounds. Three different PDMS fibres exist with a coating thickness of 7, 30 and 100 μm , respectively. Usually, 100 μm coating is used due to its higher extraction capacity. However, for higher boiling compounds with high distribution constants and long equilibration times, the thinner coatings should be used. The 7 μm coating has the advantage that it is chemically bonded and can be used at temperatures up to 340°C.

Extraction Parameters

Reliable quantitative analysis can be performed under nonequilibrium conditions, but the sensitivity will be

Table 1 SPME fibres and their recommended use

<i>Fibre coating material</i>	<i>Abbreviation</i>	<i>Recommended use</i>
Polydimethylsiloxane	PDMS	Nonpolar compounds
Carboxen/polydimethylsiloxane	Carboxen/PDMS	Very volatile compounds
Polyacrylate	PA	General
Polydimethylsiloxane/divinylbenzene	PDMS/DVB	General
Carbowax/divinylbenzene	CW/DVB	Polar compounds
Carbowax/templated resin	CW/TPR	Polar compounds

better when the extraction time is sufficient to reach near-equilibrium. The equilibration time can be shortened by agitation or heating of the sample which increase the diffusion rates. Normally, an extraction time comparable to the time of the chromatographic analysis is chosen in order to maximize sample throughput. Rapid stirring using a magnetic bar is efficient, but may not always be very reproducible; vibration of the fibre is a valid alternative for small samples. At higher temperatures the equilibration will proceed faster due to the higher diffusion rates; however, the amount adsorbed at equilibrium will be lower.

An internally cooled SPME device has been developed for the purpose of maintaining favourable distribution constants while extracting from a heated sample. Sample heating may be necessary to release analytes that are adsorbed on solid matrices. Addition of a salt normally has a positive influence on the extraction efficiency due to the increased ionic strength of the solution. When acidic compounds are analysed, the pH should be below the lowest pK_a value, because ionic compounds are not extracted but the lifetime of the fibre is reduced at low pH values. A methanol content of less than 1% in spiked samples does not affect the SPME process significantly. It must always be borne in mind that relatively large amounts of other compounds in a complex matrix may have a significant effect on the distribution constant.

Desorption

In case of analysis by GC, thermal desorption is performed in the injector. For analysis by LC, the injection loop is replaced by a special SPME desorption chamber and the desorption is performed in the mobile phase or a solvent mixture. It is important to

optimize the desorption parameters in order to guarantee that the fibre can be used for subsequent analysis without intermediate cleaning. This is essential for automation purposes and for trace analysis. For GC analysis, desorption should be as rapid as possible. The best injection is obtained when the desorption temperature is sufficiently high to ensure an almost complete desorption within 1 min or less. However, a longer desorption time is often required to avoid carry-over, in which case cryogenic focusing may be necessary. For LC analysis, desorption using the mobile phase is the best solution and can even be performed in the flowing mobile phase (dynamic mode) if the desorption is rapid. However, a higher content of an organic solvent is often needed to obtain a satisfactory desorption. In this case, the desorption chamber is filled with the appropriate solvent mixture and desorption takes place (static mode) before the injection is performed by switching the valve. A high content of organic solvent may adversely affect the chromatography if the initial mobile phase is much weaker. Furthermore, the SPME fibres are not very resistant to organic solvents, so the coupling of SPME with LC is still at the experimental stage.

Analysis of Aqueous Samples

Numerous successful applications of SPME for the analysis of aqueous samples have been reported. The analytical conditions are summarized in Table 2, and the results for the different classes of compounds are discussed below. In most of the studies, only spiked samples have been analysed; however, considering the limited effect of suspended solids and humic substances at levels typical for lake, river and groundwater, such environmental samples can also be analysed. In more complex sample matrices, SPME can be used to measure the freely dissolved

Table 2 Applications of SPME for the analysis of aqueous samples

<i>Compound</i>	<i>Fibre coating</i>	<i>Analysis (alternative detector for some compounds)</i>
Volatile organic hydrocarbons	PDMS	GC-MS (FID)
Halogenated volatile organic compounds	PDMS	GC-MS (ECD)
Polychlorinated biphenyls, polyaromatic hydrocarbons and heteroaromatic compounds	PDMS or PA	GC-MS (ECD, FID)
Phenols and nitro-compounds	PA or more polar	GC-MS (ECD)
Organochlorine, organonitrogen and organophosphorus pesticides	PA or more polar	GC-MS (ECD, AED, NPD)
Fatty acids, phenoxy acid herbicides and amines	PA or PDMS/DVB	Derivatization/GC-MS (ECD, FID)
Organometallics and inorganic metal ions	PDMS	Derivatization/GC-MS
Phenoxy acid, sulfonyleurea, phenylurea, carbamate and other polar herbicides	CW/TPR	LC-ESI/APCI-MS (UV, DAD)

Abbreviations: MS, mass spectrometry; FID, flame ionization detection; ECD, electron capture detection; AED, atomic emission detection; NPD, nitrogen and phosphorus detection; ESI, electrospray ionization; APCI, atmospheric pressure chemical ionization; UV, ultraviolet absorption; DAD, diode array detection.

compounds. While the traditional techniques extract the total amount, only a small amount is extracted by SPME, so the equilibrium with the matrix is not perturbed. By addition of an internal standard, e.g. a deuterated surrogate, the total concentration and the distribution of the analytes can be determined. Unless an isotope-labelled analogue of the analyte is used, the benefit of an internal standard in SPME analyses is very limited because even similar compounds may behave differently in the SPME process.

Volatile Organic Hydrocarbons

The analysis of benzene, toluene, ethylbenzene and *m*-, *o*- and *p*-xylene (BTEX compounds) by SPME has been studied extensively. Many other gasoline and fuel-related hydrocarbons have also been analysed. Generally, the standard deviation of replicates is around 5% and detection limits are in the low $\mu\text{g L}^{-1}$ range for the lightest compounds down to low ng L^{-1} level for the higher boiling analytes with the PDMS fibre coating.

Halogenated Volatile Organic Compounds

Numerous applications of SPME for the analysis of halogenated volatile organic compounds have been reported. The PDMS fibre coating performs well for these compounds. The precision and sensitivity are similar to those reported for the volatile organic hydrocarbons.

Polychlorinated Biphenyls, Polycyclic Aromatic Hydrocarbons and Hetero-Aromatic Compounds

Polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) have been analysed in spiked water samples and in groundwater. The equilibration times were approximately 60 min with the PDMS fibre coating. However, detection limits in the low ng L^{-1} range can be obtained with an extraction time of only 10 min. The relative standard deviations of these analyses are around 20% for the PCBs and 10% for the PAHs. Possibly, better precision could be achieved by increasing the extraction time in order to approach equilibrium. Pyrazines and several other heteroaromatic compounds have been analysed successfully with detection limits from low $\mu\text{g L}^{-1}$ levels for the volatile analytes down to low ng L^{-1} levels for the semivolatile analytes. The precision is in the range from 3 to 14% relative standard deviation. The extraction efficiency is strongly enhanced by salt addition.

Phenols and Nitro-Compounds

Usually, salt addition has a positive effect on the extraction of phenols and nitrophenols, and for analytes with pK_a values below 7 the extraction effi-

ciency is higher at low pH values. Typically, detection limits are in the low $\mu\text{g L}^{-1}$ range and the relative standard deviations are from 5 to 12%. The sensitivity and chromatography can be improved for most of the phenols by aqueous-phase acetylation prior to extraction. Nitrotoluenes, nitroanilines and nitrobenzenes have also been analysed successfully by SPME.

Organochlorine, Organonitrogen and Organophosphorus Pesticides

In several studies, the analysis of organochlorine pesticides has been examined. Generally, equilibration times range from 30 to 90 min, detection limits are in the low ng L^{-1} range with electron-capture detection (ECD) and mass spectrometry (MS), and standard deviations vary from 5 to 20%. For the organonitrogen and organophosphorus pesticides, similar precision and equilibration times have been observed, and the detection limits are at very low ng L^{-1} level with MS and nitrogen and phosphorus detectors.

Fatty Acids, Phenoxy Acid Herbicides and Amines

Fatty acids can be analysed directly from aqueous samples by SPME. However, for short chain fatty acids the detection limits are in the high $\mu\text{g L}^{-1}$ range with the polyacrylate fibre coating and worse with other fibre coatings. However, the sensitivity can be considerably improved by derivatization. Different derivatization procedures have been examined and detection limits below $\mu\text{g L}^{-1}$ can be obtained in the best cases. Similar detection limits are obtained for phenoxy acid herbicides and amines by derivatization-SPME.

Organometallics and Inorganic Metal Ions

SPME has mainly been applied for organic trace analysis. However, a few applications for inorganic metal ions and organometallics have been reported: bismuth was extracted using an experimental SPME fibre coated with a liquid ion exchanger; aqueous-phase derivatization with tetraethylborate followed by SPME has been applied to analyse methylmercury and labile Hg^{2+} in river water, and the same derivatization approach can be used for the analysis of tin and lead. The detection limits are in the low ng L^{-1} range.

Phenoxy Acid, Sulfonylurea, Phenylurea, Carbamate and Other Polar Herbicides

SPME coupled with LC-electron spray ionization (ESI)/atmospheric pressure chemical ionization (APCI)-MS has been applied for the trace analysis of polar pesticides in spiked water samples and lake

water. Acidic, as well as neutral, priority pesticides representing all major pesticide classes can be analysed successfully with single ion monitoring (SIM) detection limits in the ng L^{-1} range. Detection limits in the low $\mu\text{g L}^{-1}$ range and standard deviations below 10% were reported when UV detection was used. Finally, SPME-flow injection-MS-MS has been developed for the purpose of rapid, target-oriented screening analysis.

Validation of Standard Methods for Routine Analysis

In order for SPME to be applied for routine analysis, two issues are very important: automation and quality assurance. Thus, an autosampler has been developed for SPME-GC analysis, and three interlaboratory studies have been performed to validate the quantitative performance of SPME. One study addressed the analysis of 12 organochlorine, organonitrogen and organophosphate pesticides at low $\mu\text{g L}^{-1}$ level in aqueous samples. In the other two studies, standard methods for the analysis of volatile organic compounds and triazine herbicides in aqueous samples were validated at low $\mu\text{g L}^{-1}$ levels and around the European limit of $0.1 \mu\text{g L}^{-1}$ for individual pesticides in drinking water. Subsequently, both methods were presented by the Italian Standardization Organization, Unichim. The validations were performed in accordance with the International Standardization standard method 5725-1994 concerning interlaboratory statistics. The results regarding accuracy and precision are given in Table 3. The 95% confidence interval of the gross average of the reported results always included the true concentration of the test sample, i.e. the accuracy of the methods was very good. The precision obtained would meet the requirements for most routine analyses.

In Situ Measurements

Many well-established extraction techniques have been applied for the analysis of groundwater samples

from wells. These methods require pumping of the groundwater to the surface, sampling into appropriate containers, and transport to the analytical laboratory. Sample loss and sample composition variation may occur during these steps. Thus, a number of downhole sampling devices have been developed. However, each has limitations with respect to flexibility of sample type and sample size, maximum operating pressures and depth, portability and adaptability to difficult field conditions. The characteristics of SPME make it ideal for field sampling, i.e. it is simple, robust, portable, independent of sample volume and instrument configuration, and it is impossible to plug the fibre with particulate matter. Thus, SPME sampling probes have been developed for use in monitoring wells (Figure 1) and for fitting to the head of a cone penetrometer. They were tested in a mobile laboratory for on-site measurements of volatile organic compounds in groundwater and soil gas. Comparison of results obtained by *in situ* SPME and SPME after traditional sampling from the same groundwater wells confirmed the feasibility of the *in situ* sampling approach. Slightly lower results were obtained in most cases after traditional sampling.

Solid Samples

The major complication in the analysis of soil samples is the strong sorption of the analytes to the matrix. A nearly complete exhaustive extraction could be achieved for the BTEX compounds from sand and clay matrices by heating the sample and using an internally cooled SPME fibre for the extraction. However, in the case of less volatile and more polar analytes, the sorption is stronger and the recovery is very dependent on the organic carbon content of the soil. Thus, calibration using a model matrix would only be acceptable for screening purposes, while calibration by standard addition is needed for reliable quantitative analysis. Addition of water to the sample helps to release the analytes from the sample matrix and improves the recoveries drastically. A nearly complete extraction of polyaromatic

Table 3 Interlaboratory validation of SPME for quantitative analysis

Analytes	Number of participating laboratories	Concentration of the test sample ($\mu\text{g L}^{-1}$)	Accuracy	Average repeatability (%)	Average reproducibility (%)
Volatile organic compounds	12	3	True values within confidence intervals	9.3	28.7
Organochlorine, organonitrogen and organophosphorus pesticides	11	2-25	True values within confidence intervals	11.5	28.3
Triazine herbicides	8	0.05-0.12	True values within confidence intervals	9.6	13.6

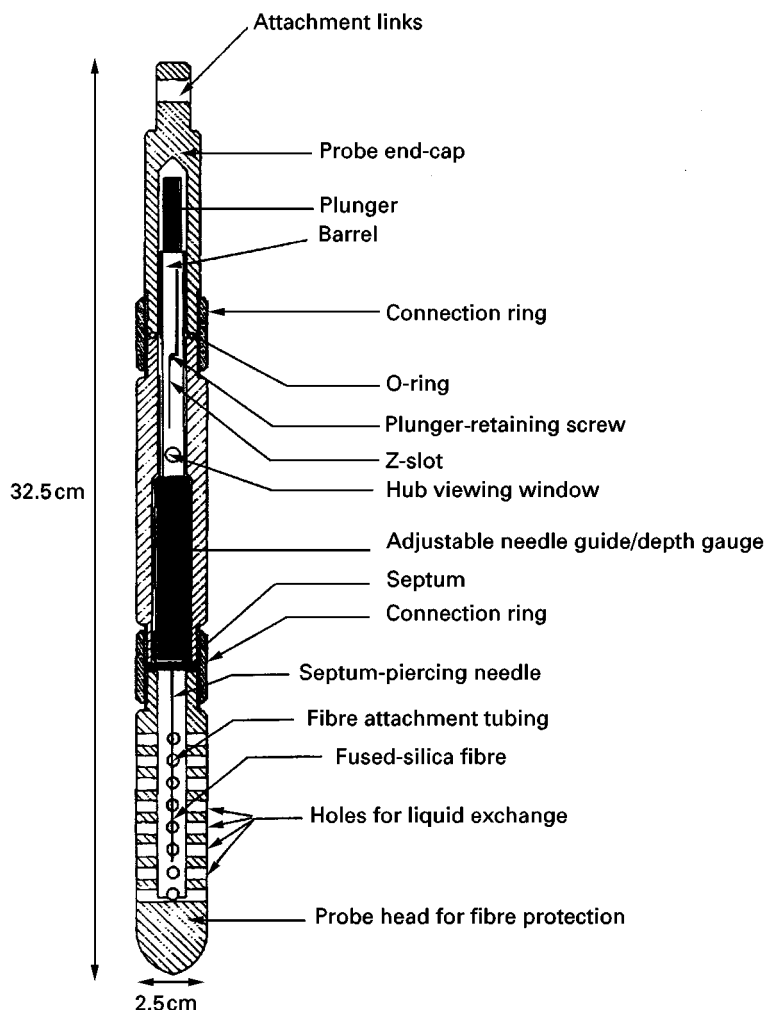


Figure 1 SPME probe for *in situ* groundwater sampling from wells. (Reproduced with permission from Nilsson *et al.*, 1998.)

hydrocarbons from different soils has been achieved by high temperature or subcritical water extraction. Finally, the leachability of pesticides from soils has been studied by SPME.

Conclusion

SPME has successfully been applied for the quantitative analysis of most of the organic, environmental priority compounds, which can be analysed by GC, in aqueous samples. In more complex sample matrices, such as wastewater and soils samples, quantitative analysis by SPME may be difficult because matrix effects influence the distribution constants significantly. Standard methods have been developed and validated regarding sensitivity, precision and accuracy for the trace analysis of volatile organic compounds and several classes of pesticides in aqueous samples. Derivatization/SPME-GC and SPME-LC have been applied for the analysis of more polar

organic compounds. However, further development of these methods is needed before they can be applied for routine analysis. Especially, further research on the coupling of SPME and LC-MS may allow many new environmental applications. Inorganic metal ions and organometallics have been analysed as well, and the use of an ion exchange fibre coating may allow more applications in this field. The small volume and the noninterfering character of SPME are important factors for numerous applications. Finally, the easy handling and simple design make SPME a good choice for in-field analytical work.

See also: II/Extraction: Solid-Phase Microextraction.

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Soxhlet Extraction

M. D. Luque de Castro and L. E. García Ayuso,
University of Córdoba, Córdoba, Spain

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The health of our environment is now a matter of great concern. This has stimulated an intensive search for an understanding of both the ways in which the natural environment works and the anthropogenic actions that bring about environmental changes. A large number of studies have been, or are in the process of being, developed in order to increase our knowledge of the processes causing environmental pollution and to propose clean analytical methods for monitoring and subsequent control. Thus, a high percentage of the studies developed so far fall within the field of analytical chemistry. There are a number of stages involved in any analytical method: definition of the aim, selection and establishment of an appropriate method, sampling plan, sample collection, sample handling and pretreatment, final measurements (detection/determination), method validation, assessment and interpretation of the results and, finally, safety.

In spite of the evolution of analytical techniques involved in some of the above mentioned stages (particularly detection/determination), the development

of some of these has not been as great as desirable. These steps constitute 'critical points' of an analytical method and, consequently, the main source of errors. The pretreatment step (including separation techniques) can be considered as a 'critical step'. Conventional Soxhlet extraction is currently one of the most frequently used pretreatment techniques, not only in environmental analysis, but also in many other fields. Its principles, performance, environmental applications and improvements are considered in more detail below.

Principles of Conventional Soxhlet Extraction

Soxhlet extraction is a very useful tool for preparative purposes in which the analyte is concentrated from the matrix as a whole or separated from particular interfering substances. Sample preparation of environmental samples has been developed for decades using a wide variety of techniques. Solvent extraction of solid samples, which is commonly known as solid-liquid extraction (also referred to as leaching or Lixiviation in a more correct use of the physicochemical terminology), is one of the oldest methods for solid sample pretreatment. Conventional Soxhlet extraction remains as one of the most