Environmental Applications

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Introduction

Solid-phase microextraction (SPME) was first described by Pawliszyn and co-workers from the University of Waterloo in 1989 and has rapidly become a popular extraction method in research.

Briefly, SPME uses an immobilized liquid polymer phase coated on the outside of a fused silica fibre. By dipping this fibre into either a liquid (usually aqueous) sample, or the headspace above a liquid sample, absorption of the analytes from the matrix into the polymer layer occurs. Analyte desorption occurs in either the heated inlet port of a gas chromatograph or a specially constructed inlet loop in the case of liquid chromatographic analysis.

Adjustment of the sample pH or ionic strength can be used to enhance the analyte partitioning into the fibre coating. The adjustment of ionic strength is commonly carried out by the addition of an inorganic salt such as sodium chloride. To reduce the time taken for equilibrium between the fibre coating and the sample agitation is used. This is usually achieved with a magnetic stir bar system.

SPME has the advantage that it is a solvent-free technique, which reduces both environmental pollution and sample preparation time, as no additional concentration step is required. There is no packed cartridge bed, as with solid-phase extraction (SPE), and so SPME does not suffer from plugging and is complete in two stages. This minimizes the chance of analyte loss or operator error.

There are now many examples of the extraction of analytes of environmental interest. This article will cover the more recent examples from each class of environmental pollutants. Articles listed in the Further Reading cover these areas in more depth than is possible here.

Volatile Organic Chemicals

One of the most common environmental applications of SPME is the analysis of volatile organic compounds. The chemicals frequently used as representative of this class are benzene, toluene, ethylbenzene and the xylene isomers (BTEX).

Most BTEX extractions have been carried out using polydimethylsiloxane (PDMS) as the polymer coating on the fibre. Whilst PDMS works well for the extraction of the BTEX compounds, the recoveries from the sample are typically in the 0.1–10% range. With such a low recovery, the limits of detection (LOD) are often higher than those achieved with conventional purge-and-trap analysis.

An interesting way to reduce LODs without resorting to more expensive detectors is to use a fibre freshly coated with PDMS that is then dipped in extra-fine powdered activated charcoal. The total thickness of this coating is approximately 100 μm, which is similar to the thickness of a commercially available fibre.

Using the PDMS/charcoal-coated fibre, recoveries of greater than 90% are achieved in about 15 min extraction time at 25°C, or in under 10 min at 75°C using headspace analysis and salting out of the sample, as illustrated in **Figure 1**. These high recoveries give LODs of $\leq 21\ \mathrm{pg\ mL^{-1}}$ with GC analysis using a flame ionization detector (FID). This is over an order of magnitude better than the LODs for the US Environmental Protection Agency method 524.2, and two orders better than conventional PDMS SPME with gas chromatography (GC)-FID analysis.

Surfactants

Alkylphenol surfactants are becoming of increasing concern due to their possible role as endocrine disrupters. SPME analysis of this class of surfactants eliminates the need for the concentration step frequently required with conventional liquid–liquid extraction or SPE.

As alkylphenol ethoxylate surfactants are not amenable to GC analysis without derivatization, and SPME with derivatization is a much less well-developed technique than classical SPME, analysis of the surfactants has been accomplished by normal-phase gradient high performance liquid chromatography (HPLC) with UV detection.

This requires a specific interface for desorping the surfactants from the fibre after adsorption (**Figure 2**). The fibre desorption chamber is a three-way tee in which two outlets are connected to the injection valve and the third houses the SPME device. Flow to the tee is via stainless steel tubing (d) and back to the injection port is via poly(ether ether ketone) (PEEK) tubing (e) connected via a finger-tight PEEK union (f). The SPME device (g) is positioned in the top part of the tee. One of the problems initially encountered with this device was stripping of the fibre coating by

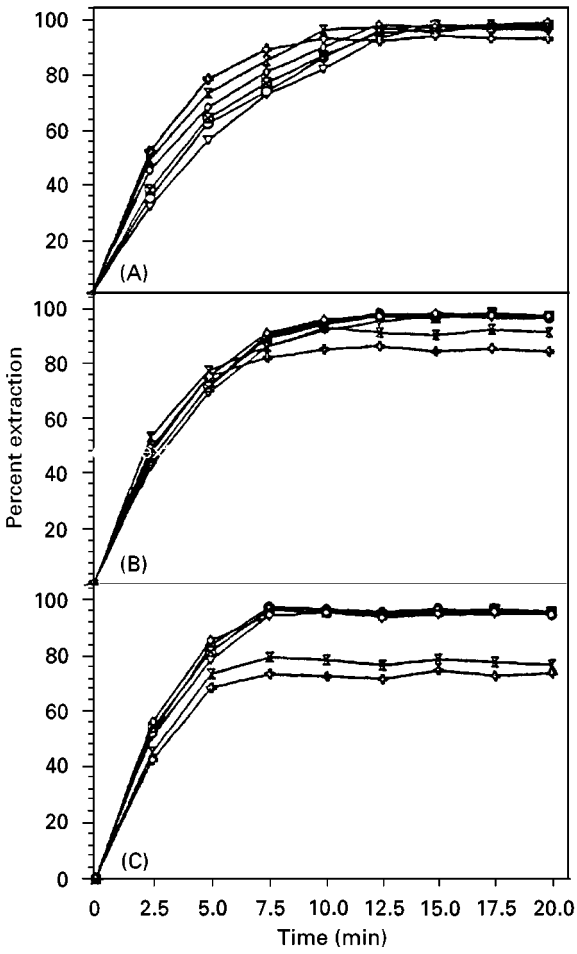

Figure 1 Dependence of extraction efficiency on exposure time and temperature. BTEX concentration, 500 pg mL^{-1} of each compound; stirring speed, 50% of maximum; amount of NaCl, 15 g. (A) $T = 25°C$; (B) $T = 50°C$; (C) $T = 75°C$. Open circles, benzene; open squares, toluene; filled circles, ethylbenzene; filled squares, *p*-xylene; open triangles, *m*-xylene; filled triangles, *o*-xylene. Reproduced with permission from Djozan DJ and Assadi J (1997). Copyright Elsevier Science.

the narrow internal diameter stainless steel tubing (d). This was because of swelling of the coating, which occurred in the desorption solvents used. Increasing the diameter of the tubing to account for this swelling solved this problem. In order to be able to withstand the high pressures used in HPLC, a slip-free supercritical fluid extraction connector (i) was used to provide a strong seal. A large diameter Teflon tube (h) and a regular ferrule (j) complete the desorption device.

When analysing for surfactants, it is important that the extraction method does not discriminate against any of the oligomers present in the sample. A Carbowax/template resin-coated SPME fibre was found to show good extraction of the various chain length surfactants. To ensure that the extracted ethoxamer distribution was the same as the original sample, salting out of the sample was carried out; without this, a bias towards shorter chain ethoxamers is obtained.

The final analysis method has been successfully applied to the determination of a number of surfactants, as shown in **Figure 3**. LODs for the individual alkylphenol ethoxamers are in the low p.p.b. range.

Hetero-organic Pollutants

Compounds with nitrogen, sulfur or oxygen (NSO) in the aromatic ring system are frequently encountered as pollutants in groundwater. These hetero-organic pollutants are often the result of creosote contamination. For NSO groundwater analysis, LODs in the ng L^{-1} range are required. Currently this is only achievable with liquid–liquid extraction using a concentration step.

For SPME analysis of NSOs, out of three fibre coatings investigated, PDMS, polyacrylate (PA) and Carbowax, only the PA coating successfully extracted all of the 15 NSO compounds investigated. However, the amount extracted at equilibrium is small, ranging from 0.4% for pyrrole to 57% for dibenzofuran. Although pH over the range of 7–10 does not affect the amount extracted, higher pH values degrade the fibre coating. Adjusting the sample ionic strength by adding sodium chloride increases the amount extracted.

The LODs obtained, distribution coefficients and aqueous solubility of the NSO compounds investigated are shown in **Table 1**. In comparison to a conventional analysis this SPME method showed improved performance for water soluble and semivolatile NSOs, but poorer performance for the volatile NSOs. Carryover from one sample to the next was also a problem and necessitated a 10 min offline fibre cleaning process between samples. Fibres were found to degrade slowly with use, and were discarded after 50 analyses.

Pesticides and Herbicides

The monitoring of groundwater for pesticide and herbicide contamination is a common environmental analysis. Accordingly, there have been a number of reports on the use of SPME for pesticide extraction. Many different classes of pesticides have been studied, including the organochlorine and organophosphorus pesticides.

With organophosphorus pesticides, the best fibre coating is an XAD polymer (polystyrene-divinylbenzene)

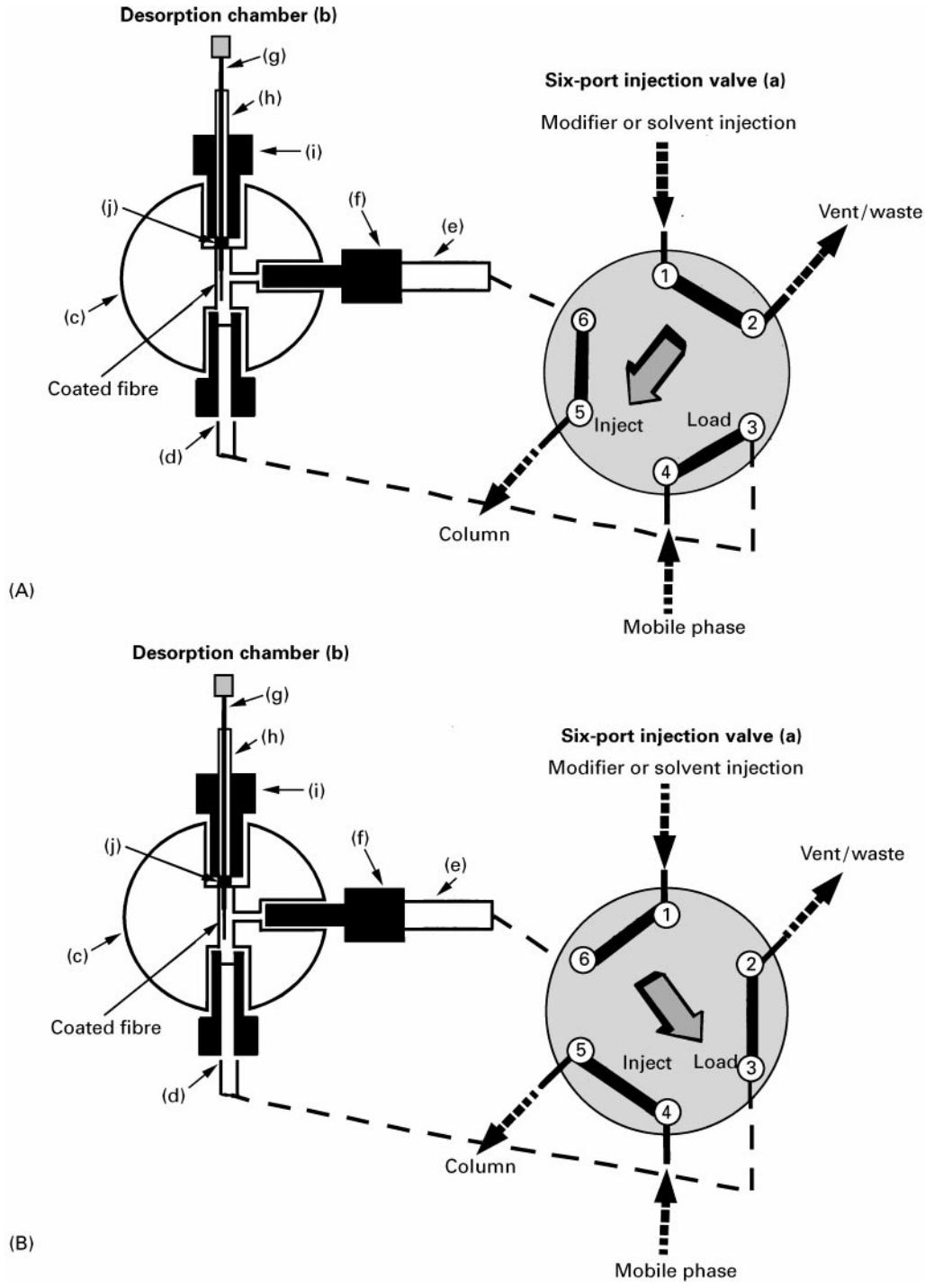

Figure 2 Modified SPME-LC interface in (A) the fibre desorption and (B) insertion modes. Arrows indicate flow direction. Reproduced with permission from Boyd-Boland and Pawliszyn (1996). Copyright American Chemical Society.

phase. The aromatic character of this material provides superior extraction for many of the organophosphorus pesticides in comparison to a PDMS phase. This class of pesticides is one group of compounds where salting out has no beneficial effect. The limitation of the SPME extraction was that the relative standard deviation (RSD) values seen were very large – up to 80% in some cases. In addition, some carryover from run to run was experienced. Until these problems can be solved, the method is more suitable for screening than for routine analysis.

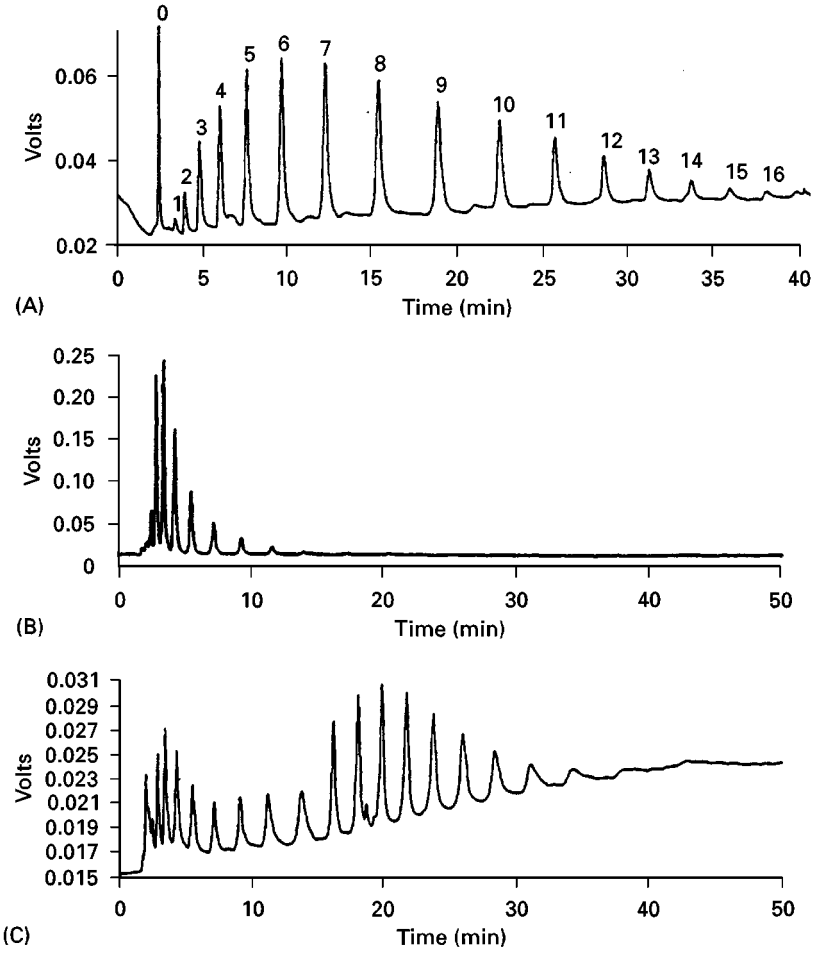

Figure 3 LC chromatograms of the extracted alkylphenol ethoxylates: (A) Triton X-100; (B) Rexol 25/4; (C) Rexol 25/5. Peak assignment in (A) refers to the number of units in the ethoxylate chain. Reproduced with permission from Boyd-Boland and Pawliszyn (1996). Copyright American Chemical Society.

One of the great areas of potential for SPME is automated analysis. This has been partially demonstrated in the field of pesticide analysis by coupling SPME extraction from a flow cell with GC-FID. The online flow-through cell used is shown in **Figure 4**. The extraction is performed whilst pumping the sample in a closed loop for 30 min. Changing the flow rate from 0.1 to 10 mL min^{-1} did not affect the precision of the extraction, presumably because flow inside the extraction chamber where the fibre is positioned is turbulent across this entire range. Method precision was found to compare well with other sample agitation methods, such as fibre vibration or magnetic stirring.

This method has been applied to the analysis of the S-triazines (herbicides) and, although not fully automated, as operator intervention was required to transfer the SPME fibre from the extraction cell to the GC, it is clearly a step in that direction.

Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls

Many of the samples analysed for environmental contamination are solids, in particular soils and sludges. These present a challenge to SPME, particularly in the case of semivolatiles, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), where heating and headspace extraction cannot be used.

A solution to this problem is first to extract the analytes of interest with subcritical water and then extract the resulting subcritical water solution via SPME. In this way, no hazardous solvents of any kind are used during the extraction procedure.

Extractions are carried out in a heavy-duty stainless steel pipe partially filled with solid sample and approximately 3.5 mL of HPLC-grade water. Care should be taken to avoid samples which might react with water leading to pressures higher than expected.

Table 1 The measured distribution constants between polyacrylate fibre and water, the octanol–water partition coefficients (log K_{ow}), aqueous solubility (mg L^{-1}), limit of detection of NSO by SPME-GC-FID and SPME-GC-ITMS in μg L^{-1} and %RSD

Compound	*K*	*log K_{ow}*	*Sw (mg L^{-1})*	*LOD-FID (μg L^{-1})*	*LOD-MS (μg L^{-1})*	*% RSD ITMS (μg L^{-1})*
Thiphene	0.34	1.81	3600	nd.	1.0	14
1-Methylpyrrole	0.04	–	Soluble	nd.	2.5	13
Pyrrole	0.10	0.75	58 000	nd.	10	12
2-Methylpyridine	0.02	1.06	Soluble	nd.	(10)	5.9
2,4-Dimethylpyridine	0.09	–	Soluble	nd.	(10)	14
Benzofuran	3.1	2.67	–	3	0.03	4.2
Benzothiphene	7.9	3.12	130	2	0.02	5.8
Quinoline	0.46	2.03	6500	15	0.3	10
Indole	3.2	2.00	1850	2	0.02	6.9
2-Methylquinoline	0.53	2.23	–	10	0.2	3.3
Dibenzofuram	22	4.12	6.6	2	0.03	10
Dibenzothiophene	27	5.45	1.0	2	0.02	11
Acridine	7.7	3.50	46	0.5	0.02	9.2
Carbazole	29	3.71	1.2	0.5	0.02	10
DBT-sulfone	4.9	–	–	0.5	0.04	9.1

– Unknown; n.d., not detected; LOD, determined by 100 μg L^{-1} standard solutions. Reproduced with permission from Johansen and Pawliszyn (1996) Copyright John Wiley & Sons, Inc.

The sealed pipe is then heated in a GC oven for an initial extraction time period. After cooling, conventional SPME extraction using a 100 μm PDMS-coated fibre of 1.8 mL of the resulting supernatant liquid is carried out in a 2 mL vial.

Increasing the temperature of the water extraction to 250°C improved the extraction of PAHs but further increases in temperature did not improve the results. Increasing the water extraction time from 15 to 60 minutes also increased the amount of PAHs

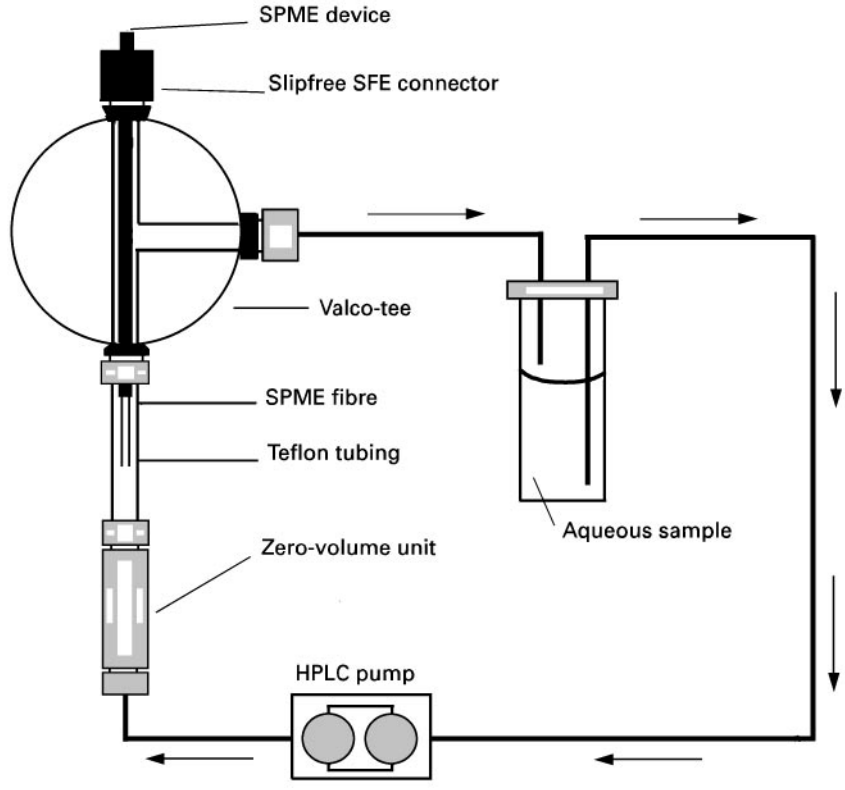

Figure 4 Instrumental set-up for the online flow-through cell. The SPME fibre hosts in a Valco-tee unit sealed by a vespel ferrule. The aqueous sample is pumped by a HPLC pump from the sample vial through the extraction cell and back to the reservoir (closed loop). Reproduced with permission from Eisart and Pawliszyn (1997). Copyright Elsevier Science.

extracted, but not by enough to justify the increased time taken for the extraction procedure. One point of note was the unusual conversion of d_{10}-anthracene to d_8-anthracene during the extraction. This was unexpected, as the hot liquid water used is regarded as being relatively unreactive and other deuterated standards did not show the same effect.

Partitioning of the higher molecular weight PAHs back on to the soil during cooling of the water extract was found to be a problem that affected quantification, unless deuterated standards for each compound were added.

PCBs are another ubiquitous environmental pollutant that have been determined by using SPME extraction in a variety of water samples. Conventional 100 μm PDMS fibres were found to give sufficient extraction of PCBs from water samples in 15 min to have a LOD of around 5 pg mL^{-1} for each congener with GC and electron-capture detection. This would allow reasonably fast screening of samples for the presence of PCBs.

Carryover was found to be present on not only the SPME fibres, but also the Teflon coated stir-bars, which were used to agitate the solution for more efficient extraction. New stir bars were required for each sample to avoid this problem. Eliminating fibre carryover was more difficult but offline desorption, coupled with running blanks between every sample, minimized the problem.

Old fibres (used more than 30 times) were found to show more severe carryover than new fibres. This degradation in use meant that even with the off-line desorption, carryover could still be present, and would necessitate regular changing of the fibre.

In contrast to many other SPME studies, it was found that no direct correlation existed between the octanol–water partitioning coefficient (K_{ow}) and the fibre-water coefficient (K_{SPME}). The deviations begin to occur with analytes of molecular mass greater than 200 and, hence, for these compounds, K_{ow} cannot be used to estimate K_{SPME}.

Suspended solids in real water matrices were found to reduce the aqueous PCB concentration by up to 50% after spiking within 24 h. This partitioning on to suspended solids is similar to that seen for PAHs.

Chlorobenzenes

Chlorobenzenes are classified as priority pollutants in both the US and the European Union. SPME has been evaluated in both the headspace sampling and direct sampling modes for the determination of chlorobenzenes in soil samples. One of the problems of using SPME with soil samples is that quantification problems occur with soil samples that have a high organic content when using the external calibration method. This has necessitated the use of the standard addition method for reliable quantitation.

Another problem with heavily contaminated soils is the overloading of the detector beyond the linear dynamic range by the large amount of analyte extracted. This is a particular problem with detectors such

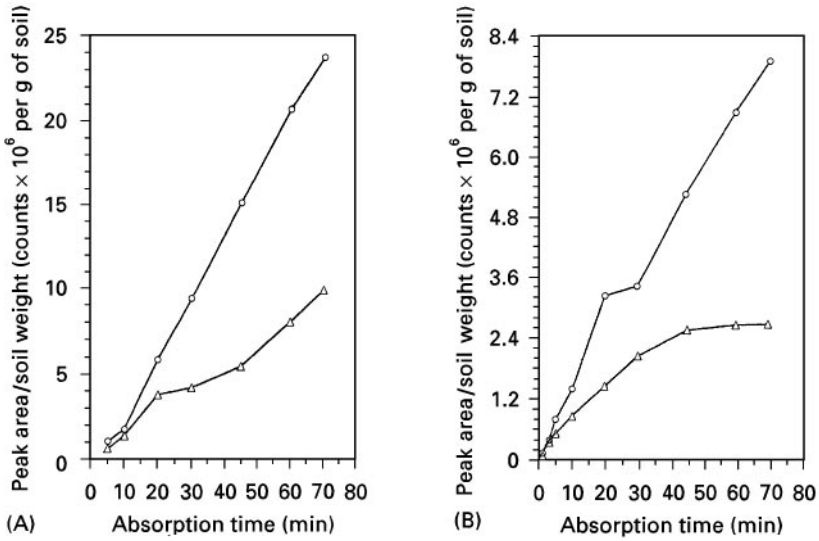

Figure 5 Effect of (A) (circles; 10%; triangles, 30%) methanol and (B) (circles, 20%; triangles, 30%) acetone on the absorption time profile of pentachlorobenzene by direct SPME-GC-ITMS using a 100 μm PDMS fibre with 0.030 g of soil, 40 mL of water–organic solvent; stirring speed 1000 rpm, sampling temperature 30°C, exposure time 25 min; splitless injection mode. Reproduced with permission from Sarrión *et al.* (1998). Copyright Elsevier Science.

as the ion trap mass spectrometer (ITMS). The addition of a water-miscible solvent, such as acetone (up to 30% v/v), to the water, which has previously been added to the soil sample, reduces the amount extracted into the fibre to within the liner dynamic range of the ITMS. The organic solvent also reduces the time required to reach equilibrium and allows shorter extraction times to be used. This is illustrated in **Figure 5**.

Using a 100 μm PDMS fibre, there was no significant difference seen in RSD values between headspace and direct sampling. A 7 μm PDMS fibre did show higher RSD values than the 100 μm PDMS fibre for headspace sampling. Using GC-ITMS analysis, the LODs were between 30 and 100 pg g^{-1} for the 100 μm fibre and headspace sampling. Headspace sampling gave a cleaner extract and resulted in a longer fibre life than the direct sampling method.

Comparison of SPME results obtained on a reference soil (CRM-530 or industrially contaminated clay soil) with results from other laboratories, mostly using Soxhlet extraction, showed good agreement for the mean values of the analytes.

Organometallics

Most SPME applications in the environmental field have been with organic pollutants. With the use of derivatization SPME, this has recently been extended to include some organometallic pollutants.

For heavy metals there is a strong dependence of the toxicity with the chemical form and the speciation of an element in a sample.

Sodium tetraethylborate ($NaBEt_4$) is a useful derivatizing agent for a number of organometallic compounds, including those of lead, mercury, cadmium, tin and selenium. Using this reagent, derivatization can be performed in aqueous solution simultaneously with the extraction.

Table 2 Reproducibility and limits of detection for tin using SPME-GC-ICPMS

Component	*RSD (n = 10) (%)*	*LOD (3 s, n = 10) (ng L^{-1} as metal)*
Monobutyltin	5.2	0.34
Dibutyltin	8.9	2.1
Tributyltin	14	1.1
Methyl mercury	11	4.3
Trimethyl lead	8.2	0.19

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Optimal derivatization conditions were obtained at a pH of 5.3 using 1 mL of a 1% $NaBEt_4$ solution with 25 mL of sample. The rate-limiting step was the extraction into the fibre coating in the headspace extraction mode and not the derivatization.

Compromise extraction conditions were used of 10 min extraction time at 25°C. Longer extraction times increase the amount extracted, but 90% is extracted within the first 10 min. Increasing the extraction temperature increased the amount extracted for some compounds, but decreased the amount for others. As a result, 25°C was chosen, as it avoids the need for sample heating.

Using GC with inductively coupled plasma–mass spectrometry (ICP-MS) detection, LODs in the low parts per trillion were obtained, as shown in **Table 2**. The method has been applied to a standard reference material (NRC PACS-1, a marine sediment) to determine organotin content. A clean extract was obtained, as can be seen in **Figure 6**. The results for the dibutyl- and tributyltin showed good agreement with

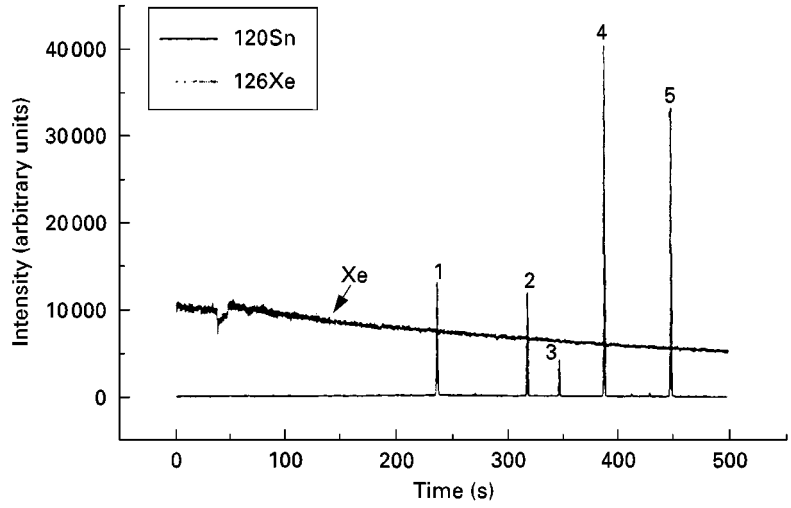

Figure 6 LC chromatogram of the PACS-1 reference material. Identification of peaks, 1, tetraethyltin; 2, monobutyltin; 3, tripropyltin; 4, dibutyltin; 5, tributyltin. Reproduced with permission from Moens *et al.* (1997). Copyright American Chemical Society.

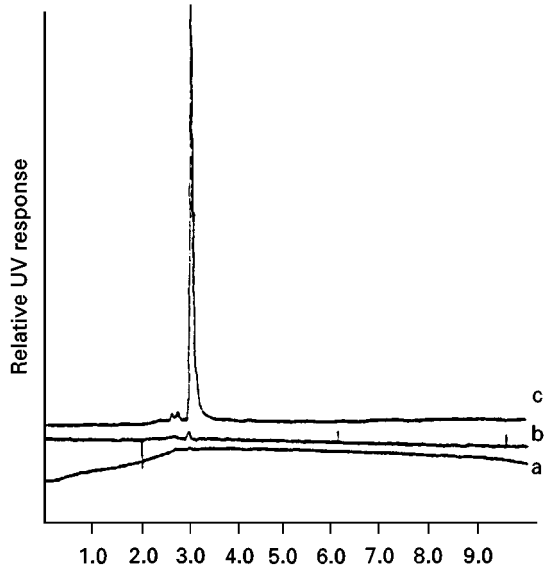

Figure 7 LC chromatogram for SPME injection with UV detection at 275 nm. (a) Fibre blank for microporous hollow fibre without dipping with DBC and $HgCl_2$ solution. (b) DBC blank microporous hollow fibre only dipping with 0.02 mol L^{-1} DBC solution for 5 min. (c) Microporous hollow fibre dipping with DBC solution for 5 min, then dipping with 0.02 mol L^{-1} $HgCl_2$ aqueous solution for 5 min. Reproduced with permission from Jia *et al.* (1998). Copyright John Wiley & Sons, Inc.

the certified values and the values obtained via a classical liquid–liquid extraction.

The values for monobutyltin were significantly higher than the certified values. This has been reported as being a problem with the derivatization using $NaBEt_4$ for monobutyltin and is not attributed to any problems with the SPME part of the analysis.

Metal Ions

Inorganic metal ion analysis has also been achieved with SPME. In order to extract metal ions from aqueous solution, an unusual fibre constructed of a hydrophobic microporous polypropylene material was used. This fibre had a film thickness of 30 μm and 30% of the surface area was covered with pores of dimensions 0.05×0.15 μm. In order to extract mercury(II) ions from aqueous solution, dibenzo-18-crown-6 (DBC) was absorbed from solution into this hollow fibre and then this DBC-filled fibre was used for the extraction.

Separation of uncomplexed DBC from the DBC-mercury(II) complex was achieved by normal-phase HPLC with UV detection. The extraction equilibrium between the fibre and the solution with DBC was reached in under 30 s. This is a very rapid equilibrium for SPME. The time to reach equilibrium for the mercury(II) ions between the treated fibre and aqueous solution was significantly longer; equilibrium was not reached after 1 h. In order to keep extraction time closer to the HPLC analysis time, 10 min extraction was used. With this extraction time and UV detection, the LOD for mercury(II) ions was around 500 p.p.b. The use of a more sensitive detection technique should significantly reduce this LOD.

The effectiveness of the extraction can be seen in **Figure 7**. No reports on the selectivity of this technique for metal ions have been published and this remains a key area for the future.

Future Developments

SPME is currently poised to become one of the major sample preparation methods for aqueous environmental samples in the future. The advantages that it offers, such as ease of use, no solvent and no plugging, make it a potential replacement for many of the liquid–liquid and SPE methods currently used. The expansion of SPME to the analysis of other analytes which are currently difficult to partition into the fibre coatings is another expected trend. This may be achieved by the development of new fibre coatings or by coupling existing coatings with derivatization or complexation reactions.

The future for SPME in the analysis of solids is less certain. Unless more robust SPME methods than those currently described are found, the replacement of Soxhlet extraction by SPME seems unlikely. Additionally, the problem of carryover is a cause for concern with the analysis of higher molecular weight analytes. Currently the cost of SPME fibres does not allow them to be used as single-use devices. This may, of course, change in the future and single-use fibres are the surest way to ensure that there is no carryover.

See also: **II/Extraction:** Analytical Extractions; Solid-Phase Microextraction; Solid-Phase Extraction. **III/Carbamate Insecticides in Foodstuffs: Chromatography & Immunoassay. Surfactants:** Liquid Chromatography. **Inclusion Complexation: Liquid Chromatography. Pesticides:** Extraction from Water. **Polychlorinated Biphenyls: Gas Chromatography. Superheated Water Mobile Phases: Liquid Chromatography.**

Further Reading

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Food Technology Applications

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Introduction

The chemicals responsible for off-flavours, malodours and taints in foods and beverages can originate from incidental contamination from environmental (outside) sources (e.g. air, water, packaging material, a contaminated ingredient) and from chemical reactions occurring within the food material itself (e.g. lipid oxidation, enzymatic action, microbial metabolic reactions). In addition, imbalance off-flavours can occur when certain ingredient components that are normally present and often essential to the product are present in abnormally high or low concentrations.

When significant off-flavour problems occur, one of the first priorities of the food chemist is to identify any volatile or semivolatile organic chemicals that may be responsible. Once the identity of the off-flavour chemical(s) has been established, it is possible to speculate on its mechanism of formation and then decide on what corrective actions to implement to eliminate recurrence of the problem in the future.

Analytical Strategy for Studying Off-Flavours

The following steps are commonly used when trying to determine which chemicals in a particular food or beverage sample are the most important contributors to off-flavours:

- Extraction of volatiles/semivolatiles. The chemicals responsible for the food taint must be extracted and usually concentrated from the food matrix. This sample preparation step is critical to success. To isolate and evaluate potential chemical components that are responsible for the food taint, analytes must be separated from interfering chemicals in the food matrix.
- Injection into the gas chromatograph (GC: with or without cryofocusing).
- Separation of extracted volatiles on a GC capillary column with a suitable liquid phase. It is not uncommon to miss important polar compounds because the chemicals do not chromatograph well on nonpolar phases. Often the extraction technique is blamed, but the problem could simply be that an inappropriate analytical capillary column was used for the separation. One example is not detecting volatile fatty acids because separation was attempted on a nonpolar column.