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Review

Solid-phase microextraction: a promising technique for sample preparation in environmental analysis

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Abstract

Solid-phase microextraction (SPME) is a simple and effective adsorption and desorption technique, which eliminates the need for solvents or complicated apparatus, for concentrating volatile or nonvolatile compounds in liquid samples or headspace. SPME is compatible with analyte separation and detection by gas chromatography and high-performance liquid chromatography, and provides linear results for wide concentrations of analytes. By controlling the polarity and thickness of the coating on the fibre, maintaining consistent sampling time, and adjusting other extraction parameters, an analyst can ensure highly consistent, quantifiable results for low concentration analytes. To date, about 400 articles on SPME have been published in different fields, including environment (water, soil, air), food, natural products, pharmaceuticals, biology, toxicology, forensics and theory. As the scope of SPME grew, new improvements were made with the appearance of new coatings that allowed an increase in the specificity of this extraction technique. The key part of the SPME fibre is of course the fibre coating. At the moment, 27 variations of fibre coating and size are available. Among the newest are a fibre assembly with a dual coating of divinylbenzene and Carboxen suspended in poly(dimethylsiloxane), and a series of 23 gauge fibres intended for specific septumless injection system. The growth of SPME is also reflected in the expanding number of the accessories that make the technology even easier to use Also available is a portable field sampler which is a self-contained unit that stores the SPME fibre after sampling and during the shipment to the laboratory. Several scientific publications show the results obtained in inter-laboratory validation studies in which SPME was applied to determine the presence of different organic compounds at ppt levels, which demonstrates the reliability of this extraction technique for quantitative analysis.

Keywords: Reviews; Solid-phase microextraction; Environmental analysis

Contents

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1. Introduction

The analytical procedure has several steps: field sampling, field sample handling, laboratory sample preparation, separation and quantitation, statistical evaluation, decision, and finally, action. Each one of these steps is important for obtaining correct results. Also, it is important to keep in mind that the analytical steps follow one after another, and the next one cannot begin until the preceding one has been completed. If one of these steps is not properly done, the overall performance of the procedure will be poor, errors will be introduced, and consequently variability in the results can be expected. On the other hand, the slowest step determines the overall speed of the analytical process, and if it is important to improve the throughput of the analysis, all steps need to be considered. If an instrument could perform all the analytical steps in the field, without human intervention, then no problems of human error would arise; but, in fact, the reality is quite different.

At the moment several sophisticated instruments are available to separate and to quantify very complex mixtures, such as gas chromatography–mass spectrometry (GC–MS) and liquid chromatography (LC)–MS. The automation and the applicability of chemometric methods to this instrumentation may be considered as very useful. In fact, traditional sample preparation methods are time and labour intensive, have multi-step procedures which lead to loss of compounds, and require the use of toxic solvents. These characteristics make such methods very difficult to combine with hyphenated and automated techniques. The result is that over 75% of analysis time is spent on sampling and preparation steps. Anything we can do to make improvements in this area will translate into advances in time saving and convenience. The phasing out of solvents constitutes a challenge to the analytical chemist in particular, and to the scientific community in general. Consequently, a great change in analytical methodology will be necessary. There is a great need for change in the current sample preparation methodology, and solvent-free alternatives are needed. These needs have driven the development of a solvent-free preparation technique: solid-phase microextraction (SP< E).

2. Sample preparation techniques

Despite the advances in separation and quantitation techniques, many sample preparation practices are based on traditional technologies such as Soxhlet extraction [1] and liquid–liquid extraction (LLE) [2] which are time consuming, labour intensive, and also require the use of toxic solvents [3]. The operating principle of any sample preparation method is to allow analytes to partition between the sample matrix and an extracting phase [4]. Sample preparation techniques which use a small quantity or no organic solvent have been available for some time. They can be classified according to the extracting phase used: gas, membrane, or solvent [5]. Table 1 shows the main steps followed in different sample preparation techniques. As we can see, LLE is a multi-step procedure that often result in loss of analytes during the process, frequently making sample preparation the major source of errors in the analysis, and making it impeditive for integration with the rest of the analytical process. Solid-phase extraction (SPE) was developed in the 1980s, and has emerged as a powerful tool for chemical isolation and purification. From trace levels to industrial scale, SPE plays an important role in a broad range of applications. SPE generically uses an adsorbent material to extract trace organic compounds from aqueous samples. It is

Table 1
Protocols used in different sample preparation techniques: liquid–liquid extraction (LLE), solid-phase extraction (SPE), and solid-phase microextraction (SPME)

LLE	SPE	SPME
·Addition of organic solvents to the sample	·Conditioning of cartridges or membranes	·Exposing SPME fibre to the sample
·Agitation in a separatory funnel	·Sample elution	·Desorption of analytes in the analytical instrument
·Separation of aqueous and organic phases	·Solvent elution to remove interferences and analyte desorption	
·Removal of organic phase	·Evaporation/concentration of the organic phase	
·Evaporation/concentration of the organic phase	·Injection in the analytical instrument	
·Injection in the analytical instrument		

limited to semivolatile or nonvolatile compounds [6] with boiling points higher than the desorption solvent temperature. It can be used in off-line and on-line modes. Compared with LLE sample preparation, off-line SPE offers reduced processing time and important solvent saving. Although automation is possible, this method still requires multi-steps, is time consuming, and presents disadvantages such as losses in the evaporation step, risks of contamination, and loss of sensitivity due to the injection of only a small aliquot of the sample. On-line methods which couple SPE sample preparation to GC or LC separation prevent the problems previously mentioned [7]. More accurate results can be expected because there is no sample handling between pre-concentration and analytical steps. Therefore, automation is easy to set up, and today several devices are commercially available. One advantage of SPE sample preparation is the stability of the adsorbed analytes allowing good storage [8]. The SPE limitations can be overcome by placing a very small quantity of the extracting phase on a fine rod made of fused-silica. The use of a small amount of liquid phase in microextraction techniques provides better performance over the large volume approach [9]. The very small geometry of this device allows fast mass transfer during extraction and desorption and prevents plugging. The conception of such a device allows a new sample preparation technique: solid-phase microextraction [10]. The SPME process has two steps: partition of analytes between the coating and the sample matrix, followed by desorption of the concentrated extract into the analytical instrument. A clean-up step is not necessary in the SPME technique because of the selective nature of coatings [11]. Thus, it can be stated that SPME was developed to make very fast sample preparation possible.

3. General considerations of solid-phase microextraction

This technique was first reported by Arthur and Pawliszyn in 1990 [11] and is now widely accepted, with constantly increasing numbers of new publications. SPME was introduced to analyse relatively volatile compounds in the environmental field, but now its use has been extended to the analysis of a great variety of matrices: gas, liquid and solid [12–17], and to a wide range of analytes from volatile to nonvolatile compounds [14–21]. The first experiments were made using optical fibres, both coated and uncoated, with liquid and solid polymeric phases [22]. Rapid development of this technique resulted in the incorporation of coated fibres into a microsyringe giving rise to the first SPME device [11]. As mentioned previously, SPME has two steps. In the first step, the coated fibre is exposed to the sample or its headspace and the target analytes partition from the sample matrix to the coating. In the second step, the fibre bearing the concentrated analytes is transfered to the analytical instrument where desorption, separation, and quantification of the extracted analytes take place. The desorption step is normally attained by placing the fibre into a hot injector in a GC instrument [23,24], or in a SPME–high-performance liquid chromatography (HPLC) interface [25,26]. Three modes of SPME can be considered: direct extraction, headspace extraction, and membrane-protected SPME. In direct extraction, the

coated fibre is directly immersed in the sample and the analytes are transported from the sample matrix to the fibre coating. To make aqueous extraction faster, agitation is necessary. For gaseous samples, natural convection of air is enough to facilitate a fast equilibration. To achieve a more efficient agitation, in the case of aqueous matrices, fast sample flow, rapid fibre or vial movement, stirring, or sonication is required [27]. These approaches are needed to reduce the effects of fluid shielding and small diffusion coefficients of analytes in liquid matrices in the zone close to the fibre. In the headspace mode, the analytes are transported to the fibre through the headspace. In this case, fibre coating is protected from damage by high-molecular-mass interferences such as proteins or humic matter. This headspace mode allows for a change in pH without damaging the fibre [28]. The membrane-protected SPME is used for the extraction of analytes in very polluted samples in order to protect the coating from damage. The comprehension of SPME theory is very important because it provides insight and leads the analyst in the right direction when developing new methods and looking for the parameters which are essential for control and optimisation. The theory of SPME has been widely presented by Pawliszyn and co-workers [28–30]. Thermodynamic aspects of this sample preparation technique have been extensively studied and show that the amount of the analyte extracted by the coating is directly proportional to analyte concentration in the sample and is independent of fibre location. This means that it may be placed into the headspace or directly in the sample, if fibre coating, headspace, and sample volume are kept constant. Distribution constants, K_{fs} and K_{hs}, can be estimated from physico–chemical data and chromatographic parameters. Thermodynamic theory predicts the effects of temperature, salting, polarity of sample matrix and coating material in order to optimise the extraction conditions with a minimum number of experiments. The kinetics of SPME determines the speed of extraction. Mathematical models that allow the determination of diffusion coefficients and boundary distribution constants have also been developed [28]. Modification of kinetic theory can be applied to a model extraction in a coating containing a high reagent concentration, allowing simultaneous derivatization and adsorption of analytes in the fibre.

4. Conditions that affect solid-phase microextraction

Most SPME methods developed until now are used in combination with gas chromatography and suitable detection. Hyphenation with HPLC methods has not been so well explored.

4.1. Coatings

Currently several coatings are commercially available: three poly(dimethylsiloxane) (PDMS) films of different thickness (7, 30 and 100 μm), 85 μm polyacrylate (PA), and the mixed phases of 65, 60 μm PDMS–divinylbenzene (DVB), 75 μm Carboxen–PDMS), 65 μm Carbowax (CW)–DVB, and 50 μm CW–templated resin (TR). In mixed phases, DVB porous microspheres are immobilized on the fibre by using carbowax or PDMS as glue to hold them together. This structure allows small adsorption discrimination as a function of analyte molecular mass (Fig. 1). The choice of a particular coating is chemical structure dependent. As a general selection rule, we can apply ‘‘like dissolves like’’; however, knowledge of other extraction and separation techniques is helpful. To date, only general coatings are available, and the needed selectivity is based on polarity and volatility differences among molecules. In addition to commercial coatings, ‘‘custom made’’ fibres have been developed for the extraction of specific analytes [31,32]. The most popular coatings to date are PDMS fibres, and whenever possible they should be used, as they are very rugged liquid coatings which are able to withstand high injector temperatures up to about 300°C. PDMS is a nonpolar phase which extracts nonpolar analytes very well [24,26,33–39]. However they can also be used to extract more polar compounds after optimising extraction conditions such as pH, salt concentration, and temperature. In the case of PDMS fibres which are commercially available in different thickness, we must choose the thinnest coating which achieves the required limit of detection (LOD) [40–42]. As a general rule, when applying direct aqueous extraction with magnetic stirring, a 100 μm PDMS coating provides equilibration times of less than 1 h for compounds which have estimated distribution constants less than 10 000 [28]. For compounds with higher constants, thinner PDMS coatings should be

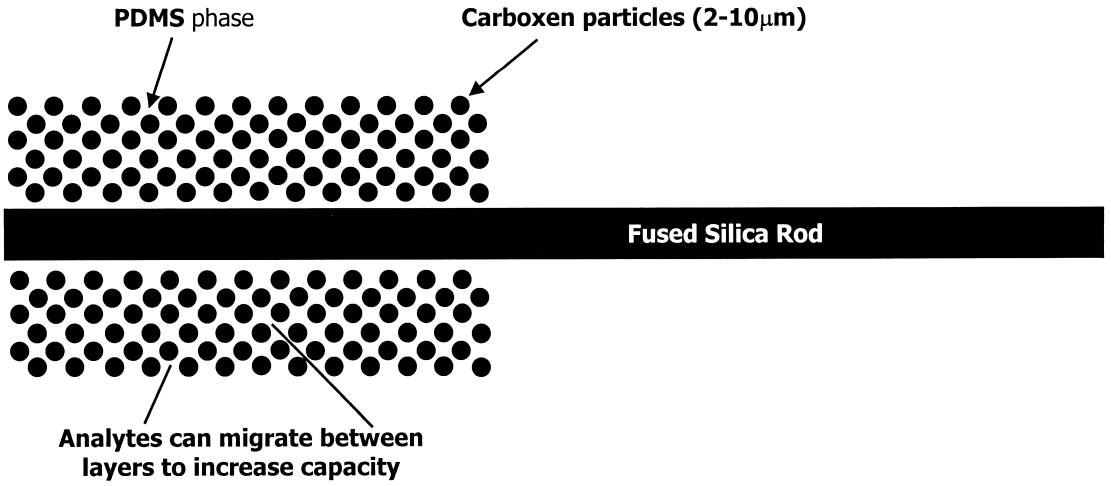

Fig. 1. Close-up view of Carboxen–PDMS fibre.

considered since the equilibration time is shorter [43]. Table 2 presents the effects of coating thickness on analyte recovery. The PA phase is suitable for more polar compounds like phenols. In this coating, diffusion coefficients are smaller than in PDMS fibres, so the extraction time is longer [21,44–46].

Table 2
Effects of coating thickness on analyte recovery[a]

Analyte	PDMS film thickness/ Ref. recovery (%)		
	100 μm	30 μm	7 μm
Benzene	2	<1	<1
Toluene	5	1	<1
Chlorobenzene	6	2	<1
Ethylbenzene	3	4	1
1,3-Dichlorobenzene	17	5	2
1,4-Dichlorobenzene	15	5	1
1,2-Dichlorobenzene	15	4	1
Naphthalene	13	4	1
Acenaphthylene	19	8	3
Fluorene	29	18	8
Phenanthrene	37	27	16
Anthracene	49	38	32
Pyrene	69	54	47
Benzo[*a*]anthracene	105	91	96
Chrysene[b]	100	100	100
Benzo[*b*]fluoranthene	104	111	120
Benzo[*k*]fluoranthene	111	124	127
Benzo[*a*]pyrene	119	127	131
Indeno[1,2,3-*cd*]pyrene	61	140	148
Benzo[*ghi*]perylene	61	117	122

[a] SPME: fibre immersed in sample, 15 min, rapid stirring.
[b] Reference value.

The mixed phase coatings have complementary properties compared with PDMS and PA. The distribution constants are typically higher when compared with PDMS, since the adsorption process on porous poly(divinylbenzene) particles is better suited for more polar compounds. These coatings have been used in the determination of aromatic amines and explosives, and the achieved sensitivity was very good [47,48]. The use of DVB template resin is advisable in order to reduce molecular mass discrimination. When target compounds have polymeric structures that vary in chain length the extracted amount will vary as a function of their size relative to the pore dimension. A DVB template resin was successfully used to determine alkylphenol ethoxylate surfactants in water [49]. The use of SPME fibres faces a set of problems when applied to HPLC [26]. In HPLC we have frequent problems concerning the design of the interface used, desorption mode, solubility of the fibre coating in the organic solvent of the mobile phase, swelling of the coating, and, flow-rate changes during desorption. As an example, to date no publication on the determination of phenols by SPME–HPLC has been made. In fact, the recommended PA fibres have a great affinity for these compounds, mainly for the more polar, but they are not released during the desorption step, with the exception of pentachlorophenol. In contrast, the performance is completely different when SPME–GC is chosen. Recently, HPLC stationary phases of 5-μm particle size C_8 and C_{18} were glued to a metal

needle. As a result, the adsorption of analytes is faster due to the greater active surface, the fibre capacity is increased, and the mechanical stability of the needle is increased [50]. In Table 3, the fibre coatings commercially available for SPME, some properties, use, and applications are presented.

4.2. Extraction conditions

The extraction procedure consists of exposing the SPME fibre to a small volume of aqueous sample or its headspace for a certain length of time. Agitation is normally used to achieve faster equilibration because it enhances the diffusion of analytes toward the fibre. Compounds with low diffusion coefficients have long equilibration times; in this case to abbreviate the analysis time, an extraction–time profile curve is constructed, showing the dependence of the amount of the analyte extracted as a function of time. The shortest acceptable time is chosen according to the analyte detection limit. Consequently the exposure time must be very well controlled to ensure good reproducibility. The extraction temperature has two opposing effects on the SPME technique. Increasing temperature enhances the diffusion coefficient of analytes; on the other hand, as the adsorption is an exothermic process, increasing temperature reduces the distribution constant of the analyte. Pawliszyn introduced a new device which allows the sample to be heated and the fibre to be cooled simultaneously. This facilitates mass transfer of analytes from the sample to the coating, increasing the efficiency of the process [28]. The pH of the sample is important for slightly acid or basic compounds (e.g., phenols and amines) because they need to be kept in the undissociated form [21,48].. However, PDMS fibres cannot be exposed to a sample with a pH below 4 or above 10 [51]. The addition of salt, usually sodium chloride or sodium sulphate, increases the ionic strength of the solution. This makes organic compounds less soluble, increasing the partition coefficients several times. Nevertheless, after the desorption the fibre must be very carefully washed because it becomes more fragile. Table 4 illustrates the effect of salt and pH on the extraction of phenols.

4.3. Derivatization on solid-phase microextraction

Derivatization may be used if very polar compounds have to be extracted. It can be performed in three ways: direct derivatization in the sample matrix, doping the fibre coating with the derivatizing reagent, and derivatization in GC injection port [52]. Within these three ways, the most interesting and potentially more useful one is simultaneous deri-

Table 3
Fibre coatings commercially available for SPME: use, some properties and applications

Fibre coating	Film thickness (μm)	Recommended use	Maximum GC injector temperature (°C)	Applications
Poly(dimethylsiloxane) (PDMS)	100	GC, HPLC	280	Nonpolar organic compounds such as VOCs, polycyclic aromatic hydrocarbons, benzene/toluene/ ethylbenzene/xylenes, organochlorine pesticides
	30	GC, HPLC	280	
	7	GC, HPLC	340	
Polyacrylate (PA)	85	GC, HPLC	320	Polar organic compounds such as triazines, organophosphorous pesticides and phenols
Poly(dimethylsiloxane)–divinylbenzene (PDMS–DVB)	65	GC, HPLC	270	Aromatic hydrocarbons, aromatic amines, VOCs
	60	GC	270	
Carboxen–poly(dimethylsiloxane) (Carboxen–PDMS)	75	GC	320	VOCs, hydrocarbons
Carbowax–divinylbenzene (CW–DVB)	65	GC	260	Polar organic compounds such as alcohols, ketones, nitroaromatics
Carbowax–templated resin (CW–TR)	50	HPLC		Anionic surfactants, aromatic amines

Table 4
Effect of salt and pH on the extraction of phenols by SPME

Analyte	No salt, neutral	No salt, pH 2	Salt, neutral	Salt, pH 2
2-Chlorophenol	1800	2361	3952	14 028
Phenol	810	1003	6425	6150
Methylphenol	761	882	5485	7434
3- and 4-Methylphenol	1795	1846	15 337	19 723
2-Nitrophenol	422	474	311	2315
2,4-Dimethylphenol	1344	1476	15 000	20 710
2,4-Dichlorophenol	5396	8138	19 803	61 664
2,6-Dichlorophenol	2991	5858	12 511	48 530
4-Chloro-3-methylphenol	2398	3137	24 060	33 529
2,4,5-Trichlorophenol	3115	11 097	24 270	96 333
2,4,6-Trichlorophenol	9702	19 307	35 466	109 492
2,4-Dinitrophenol	0	11	765	1182
4-Nitrophenol	626	730	11 458	6536
2,3,4,6-Tetrachlorophenol	3108	27 683	33 938	70 440
2-Methyl-4,6-dinitrophenol	55	47	920	1685
Pentachlorophenol	2305	40 582	22 056	143 905
Dinoseb	68	2123	6676	37 744

vatization and extraction performed directly in the coating, because it allows for high efficiencies and can be used in field applications. This procedure is limited to low volatility reagents, but if the reactive agent is chemically attached to the coating, the chemically bound product can be released at high injector temperatures. This principle was recently demonstrated by Konieczka et al. [53].

4.4. Addition of solvent

Until this time the addition of an organic solvent to the aqueous sample has not been very well studied, but it usually reduces the amount of extracted analytes [30,54]. However, the addition of organic solvent in solid and sludge samples enhances the diffusion of analytes from the sample to the fibre coating [28]. The addition of water to release analytes from the matrix has also been effective, and it is often used to increase extraction efficiency [9]. Humidity of the air can interfere with the extraction performance from the headspace, and a relative humidity of 90% can reduce the analyte adsorption by about 10% [55].

4.5. Agitation of the sample

The effectiveness of the agitation technique determines the equilibration time of aqueous samples. The agitation methods in SPME are the following: magnetic stirring – which requires a stirring bar in the vial; vortex technique – the vial is moved rapidly in a circular motion; fibre movement; flow through, and sonication. Magnetic stirring is most commonly used in SPME due to its availability in analytical laboratories and because it can be used in different SPME sampling modes. Very recently, Varian has implemented the needle vibration technique that uses an external motor in the design of a new autosampler [23]. The most effective agitation method for SPME applications is direct sonication, providing very short extraction times (20 s). This approach however presents the inconvenience of heating the sample and in some cases destroying analytes [28].

4.6. Selection of separation and detection techniques

Selection of instrumentation in order to obtain a good separation and quantitation of the analytes depends on sample complexity as well as the selectivity of the extractive process. As the available fibres are not highly selective, the demands on separation/quantitation are very high. Most SPME applications have been developed for gas chromatography, but more recently commercial interfaces to

HPLC have been designed. In the future, coupling SPME to capillary electrophoresis and supercritical fluid chromatography is expected [56]. Since, mass spectrometer detectors are used for complex environmental and biological samples, selective coatings will be very useful in the direct coupling of SPME to MS–MS and inductively coupled plasma (ICP) MS as well.

5. Solid-phase microextraction applications to the analysis of environmental samples

A great number of applications of SPME can be found in the environmental field, such as air [12,35], surface and groundwater [13,14,16,18,36,38–42,46], seawater [6,47], wastewater [17,26,34,57], and soils [44,45,58,59]. Although full removal of target analytes from sample matrix is not obtained, the high concentration ability and selectivity of this technique allows direct and highly sensitive analysis of the extracted mixtures. Combining the high concentration ability and selectivity of the fibre coating with a very sensitive detector, ppt detection limits can be achieved [39,60]. Recently SPME has been introduced as a very useful technique for field analysis [61,62]. A portable field sampler has been designed for this purpose. The manual-type holder stores the fibre after sampling by sealing it with an internal septum. Analytes can be stored for several days before starting the analysis, without significant losses (Table 5).

Table 5
Effects on chlorinated pesticides concentration after 3 days storage on 100 μm PDMS SPME fibre

Analyte	% Difference
TEPP[a]	4
Thionazin	−5
Sulfotep	−4
Phorate	−10
Dimethoate	−15
Simazine	−13
Atrazine	−5
Disulfoton	−9
Methyl parathion	−7
Malathion	4
Parathion	−1
Famphur	−9
Mean difference	−6

[a] TEPP=Tetraethylpyrophosphate.

6. Solid-phase extraction publications

According to a collection of references on SPME made by Hall, until May 1999, 416 references on this sample preparation technique could be found. Their distribution is as follows: general information articles 5%, environmental applications 40%, food analysis and botanical applications 20%, clinical and forensic applications 20%, and fundamental development 15%. Environmental applications have greater representation compared to other fields. The major application uses GC as the analytical method with specific detectors, and a small percentage (5%) uses HPLC as the analytical procedure. We can consider various explanations for this feature, but the best one is that is simpler to apply SPME to GC analysis because it was conceived for this kind of instrumentation. In HPLC, we have to face several problems which are explained in Section 4.1.

7. Inter-laboratory studies

In order to assess the applicability of SPME, some inter-laboratory studies were done. In one of them, 11 different laboratories from Europe and North America took part in the test. The test sample contained organochlorine, organonitrogen and organophosphorous pesticides at ppt levels. The repeatability, reproducibility and accuracy were satisfactory in all laboratories [63]. Two other inter-laboratory studies were made for the determination of volatile organic compounds in aqueous samples [64], and also for triazine herbicides and their degradation products at ppt level in water samples [65]. Nilsson and co-workers organised an inter-laboratory study with 20 laboratories participating to validate a SPME method for quantitative analysis of volatile organic compounds (VOCs) in aqueous samples. This validation was performed according the ISO Standard inter-laboratory studies on the basis

of certified reference materials (CRMs) use and by comparison with purge and trap and headspace (HS) techniques. The linearity was very good, and detection limits were at the ppt level with a MS detector. The accuracy was similar in the three studied analytical methods and precision was satisfactory. HS-SPME allows better precision than SPME in direct mode, but accuracy was the same in the two methods. Finally, the validation of SPME for the determination of triazine and degradation products at ppt level in water samples was also performed according to ISO rules. Good sensitivity was attained allowing for quantitation below European Union limits for individual pesticides in drinking water, and the accuracy was good in all laboratories. Also good reproducibility and repeatability were found.

8. Future analytical applications

The expansion of SPME applications is limited by the availability of appropriate instrumentation and coatings. Combining SPME with very specific detection techniques, and using a flash desorption injector it is possible to analyse organic volatiles in water samples in 3 min. The automation of this process would increase the laboratory throughput 10 times over purge and trap methods [28]. The greatest improvement over the current practice would consist in sample preparation and analysis in the field, where the sample was collected. In this way, the possibility of errors associated with the handling and storing steps would be reduced, as well as costs. In addition, a faster and better characterisation of the problem would be possible, as the analytical information will be given immediately for evaluation and decision. A new field to be explored is industrial hygiene by placing SPME devices in strategic places to monitor parameters which affect the health of workers. Fig. 2 shows the chromatogram obtained after exposing a SPME fibre to the laboratory environment. Fig. 3 shows a chromatogram obtained when water samples were analysed for trihalomethanes in the laboratory. The manipulation of organic solvents during the analytical process has resulted in a fibre coating contamination. The evaluation of biotoxicity of different environments could be another future analytical application [28]. New coatings for the selective extraction of inorganic ions from aqueous matrices for quantitation and speciation could be developed [66]. Specific extraction of very complex matrices such as biological samples could be simplified with bioaffinity coatings. Basic proteins can be extracted with a polyacrylic acid coating [67].

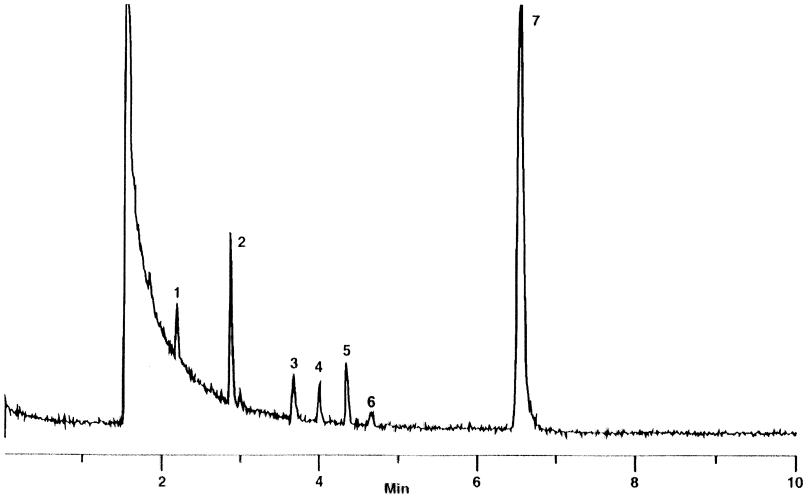

Fig. 2. Exposure of SPME fibre in a research laboratory. 1=Methanol, 2=ethanol, 3=acetone, 4=acetonitrile, 5=methylene chloride, 6=hexane, 7=isooctane.

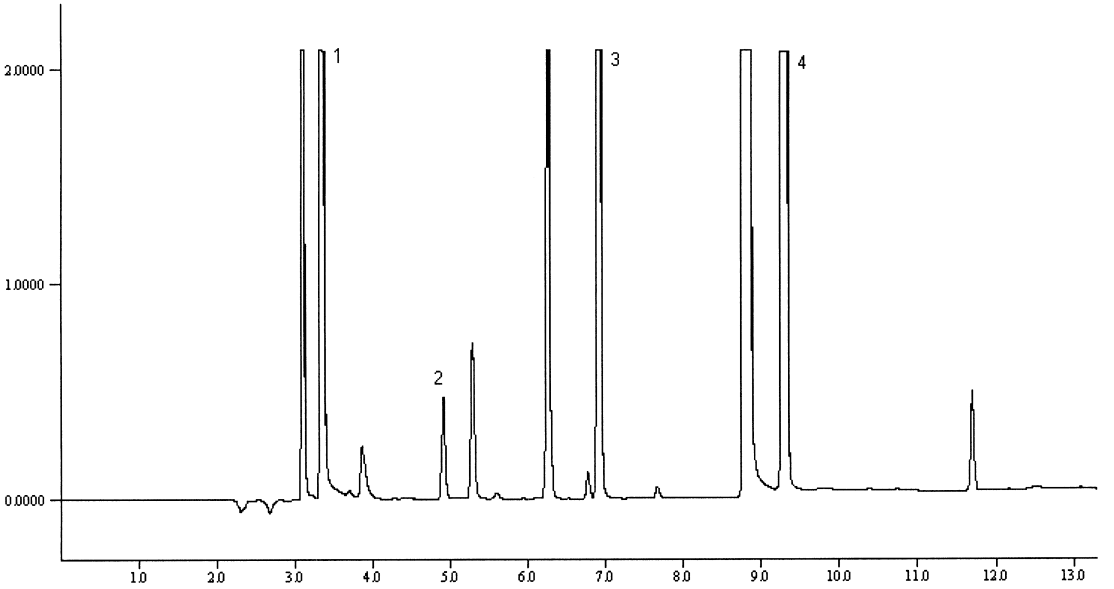

Fig. 3. Contamination of the fibre coating by laboratory environment during an automated process for determination of trihalomethanes in water samples. Trihalomethanes: 1=$CHCl_3$, 2=$CHBrCl_2$, 3=$CHBr_2Cl$, 4=$CHBr_3$. (Restek RTX-624W/Integra-Guard Column, 30 m×0.32 mm I.D., 1.8 μm film; electron-capture detector; carrier gas helium; 80°C for 5 min to 150°C at 10°C/min and hold 2 min).

9. Some limitations in solid-phase microextraction

The quality of the fibres depends on the manufacturer, and sometimes the performance is different from batch to batch. This means the need of optimisation of each fibre before use. Also fibres are fragile and can easily be broken. Conditioning should always be performed on each new fibre and also when a fibre has not been used for some time. The time required for thermal conditioning is given by the manufacturer, but even with careful conditioning some bleeding of the coating can be observed. The carry-over of the fibre is also a problem that in some cases is difficult to eliminate, even at high temperatures. Thus, blank GC or LC runs should be performed with the fibre between sampling. When a high percentage of suspended matter is present in the sample, the fibre coating can be damaged during agitation; also high-molecular-mass compounds can adsorb irreversibly to the fibre, thus changing the properties of the coating and making it unusable. In these cases, an SPME fibre protected with a membrane must be used [28]. These last two problems might be one of the reasons for the poor reproducibility and linearity that is sometimes found when extracting analytes from polluted water [26]. The formation of gas bubbles on the fibre surface is sometimes difficult to prevent, and it affects the mass transfer rates and leads to problems mentioned before. The use of an appropriate isotopically labelled internal standard, in conjunction with mass spectrometric detection, it is the most reliable solution, even though it is expensive. Some problems of sensitivity must also be noted. The sensitivity of SPME technique is proportional to the number of moles of analyte extracted from the sample. As the sample volume increases, so does the amount of analyte extracted, until the volume of the sample becomes significantly larger than the product of the distribution constant and the volume of the coating (fibre capacity; $K_{fs} \cdot V_f << V_s$). At this point, the sensitivity of the method does not improve with a further increase in volume. On the contrary, in LLE or SPE the sample volume can be manipulated to improve sensitivity. Still, the need for high volumes of collected samples makes the transportation and storage steps very critical.

10. Conclusions

SPME methods are still in the development stage. Its appearance in the 1990s stimulated the curiosity of the scientific community and a certain acceptance took place. In fact, the advantages were very attractive to laboratory chemists who sought better conditions in their routine work.

A sample preparation method that was fast, simple, solvent-free, inexpensive, versatile, sensitive if connected in-line with GC, selective if connected to GC–MS, allowable for small sample volumes, and sample-matrix ''independent'' until then seemed almost impossible to realize.

The number of scientific papers on SPME has increased rapidly and still continues to increase. The challenge is to explore the solvent-free feature, speed of extraction, convenient hyphenation, and automation. Although only a few optimisation parameters have been completely explored, the results obtained to date are very promising and represent the potential scope of success in future applications. Despite the existing drawbacks in this preparation technique, the availability of new fibre coatings that extend the range of applications to other groups of compounds, as well as more advanced features and application of field devices, demonstrate that SPME is a good alternative to the traditional extraction techniques.

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