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Review

# Polyethylene glycol-coated solid-phase microextraction fibres for the extraction of polar analytes—A review

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ABSTRACT

The article discusses the merits and limitations of commercially available solid-phase microextraction (SPME) fibres and compares them with the new type of extraction coatings, in particular those containing polyethylene glycol as sorbent, as well as the methods of the preparation of the latter. It also analyses their possible application for the extraction of a broad spectrum of analytes, with particular emphasis on the sampling of polar organic compounds from different media.



**Contents**



## 1. Introduction

One of the most important challenges facing contemporary analytical chemistry is the determination of a wide range of analytes in samples of media with a complex matrix composition. It has also become imperative that new analytical methodologies should comply with the principles of sustainable development and green chemistry. Unfortunately, however, most analytical techniques are insufficiently sensitive for the direct determination of analytes present in trace or ultratrace amounts; moreover, in many cases, the analytes have to be separated from the matrix before the proper analysis can commence.

The sample preparation step is of fundamental importance for the accuracy and reliability of the final analysis results. This

*Abbreviations:* BTEX, benzene, toluene, ethylbenzene, xylenes; CAR, carboxen; CE, capillary electrophoresis; CV, cyclic voltammetry; CW, carbowax; DVB, divinylbenzene; GC, gas chromatography; HPLC, high performance liquid chromatography; HS-SPME, headspace solid-phase microextraction; ICP, inductively coupled plasma; MAH, monocyclic aromatic hydrocarbons; MESI, membrane extraction with sorbent interface; M-SPME, membrane solid-phase microextraction; P3DDT, poly(3-dodecylthiophene); PA, polyacrylate; PAH, polycyclic aromatic hydrocarbons; PANI, polyaniline; PCB, polychlorinated biphenyls; PDMS, polydimethylsiloxane; PEG, polyethylene glycol; PEO, polyethylene oxide; PPy, polypyrrole; SFC, supercritical fluid chromatography; SPME, solid-phase microextraction; VOC, volatile organic compounds.

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**Table 1**
Manufacturer's recommendations and examples of applications of commercially available extraction coatings.

| Type of SPME fibre | Analytes | Example of use | Determination technique |
|---|---|---|---|
| 100 μm PDMS | Volatiles (MW 60–275) | VOC, BTEX, chlorobenzenes [37], PAH, MAH [38,39], pesticides, triazines, herbicides [40,41], PCB [42] | GC/HPLC |
| 30 μm PDMS | Non-polar semi-volatiles (MW 80–500) | PAH [38,39] | GC |
| 7 μm PDMS | Non-polar high molecular weight compounds (MW 125–600) | PAH [38,39] | GC |
| 65 μm PDMS/DVB | Volatiles, amines, nitro-aromatic compounds (MW 50–300) | VOC, BTEX, chlorobenzenes [35,43], PAH [39], aromatic amines, ketones, alcohols, aldehydes, terpenes [44] | GC |
| 75/80 μm CAR/PDMS | Gases and low molecular weight Compounds (MW 30–225) | VOC, BTEX, chlorobenzenes [45], PAH, MAH [39], metals*: arsenic, selenium, antimony, tin [46] | GC, *ICP |
| 50/30 μm DVB/CAR/PDMS | Flavour compounds: semi-volatile, volatile, C3–C20; trace compound analysis (MW 40–275) | PAH, MAH [39] | GC |
| 85 μm PA | Polar semi-volatiles (MW 80–300) | Pesticides, triazines, herbicides [40,47,48], phenols [49,50] | GC, HPLC |
| 60 μm PEG (CW/DVB) | Alcohols, polar compounds (MW 40–275) | Aromatic amines, ketones, alcohols, aldehydes, terpenes [34,51] | GC |

* Indicates that for metals, ICP was used as the determination technique.

has required the implementation of new, less time consuming methods, especially solventless/solvent free sample preparation techniques. One of the most commonly used solventless sample preparation techniques is solid-phase microextraction (SPME) [1]. An SPME device consists basically of a silica fibre or metal core, coated with a thin layer of a suitable polymeric sorbent or immobilized liquid, fixed within the needle of a syringe-like arrangement. Extraction is performed by immersing the fibre in a gaseous medium or a relatively pure liquid medium; analytes can also be sampled from the headspace (HS-SPME) [2]. Headspace sampling is particularly useful for analysing the composition of solid samples or samples containing matrix constituents that could contaminate or damage the fibre (e.g. petrochemical samples, high-molecular weight compounds, humus compounds [3]) and in the extraction of very volatile analytes such as PAHs, BTEX and VOCs [3,4]. On completion of the extraction the fibre is placed directly in the injector of the monitoring instrument (usually GC, but can also be HPLC [5–7], CE [8] or SFC [9]), where desorption of the analytes absorbed on the fibre takes place [10].

SPME is used to sampling a wide range of volatile and medium volatile analytes from gases, liquids and solids with a diverse matrix composition (environmental, biological, contaminated, suspended samples) [11–15]. The technique's great popularity is due to its many merits, the most important of which are as follows:

- simplicity of operation,
- relatively short extraction time,
- lack of artefacts,
- no need of expensive or complex equipment,
- possibility of full automation,
- easy interfacing with GC systems,
- applicability to both *in situ* and *in vivo* sampling.

SPME has many advantages and a broad field of application, and so much research work has been aimed at improving recoveries and enhancing the sensitivity of the method: this has led to the development of completely new constructional approaches, for example, a fibre with internal cooling [16–18] or in-tube SPME [19], as well as modifications of existing techniques, mainly through their miniaturization and automation [20,21]. Aside from this, work is also in hand to examine the dependence of analyte recovery on process parameters (extraction fibre structure, extraction temperature and time, method of stirring etc. [22–26], or additional processing of the medium under scrutiny [27–30]).

In its basic form, however, SPME has certain limitations: it is not very selective, the fibre is mechanically weak, and only a small selection of extraction fibre coatings is commercially available. In addition, recoveries (sample-to-fibre) are relatively low, particularly of polar analytes sampled from matrices with polar constituents. Work is therefore under way to develop mechanically stronger and thermally more resistant fibres, as well as new sorbents for possible implementation as polar SPME fibre coatings. To increase the affinity of sorbents for polar analytes, more polar sorbents as extraction coatings ought to be used. But this would result in an equally enhanced affinity for the polar constituents of the sample matrix and could lead to competing adsorption processes, and eventually to the analyte being leached out of the extraction fibre. Such an approach is thus a non-starter. SPME fibre coatings usually take the form of immobilized liquids like non-polar PDMS and the highly polar PEG [31].

If SPME is used to sample alcohols and the most polar compounds with molecular masses from 40 to 275, manufacturers recommend using a PEG fibre as the sorption phase [32]. PEG is a particularly interesting material since for small molecular masses it is a pseudoliquid; analyte retention is thus by absorption or dissolution in the extractant. In contrast to adsorption, absorption permits the release of analytes from the extraction fibre coating at low temperatures; compounds with a low degradation temperature will therefore not decompose. In addition, PEG is thermally highly stable, has short extraction and analyte desorption times, and gives excellent recoveries of polar analytes. This material is therefore of increasing interest to analysts in their search for highly selective sorbents, which can be employed as polar stationary phases in extraction techniques for sample preparation.

## 2. SPME fibre coatings

Even a cursory glance at the literature reports on SPME shows that the method's poor selectivity and the limited choice of extraction fibre coatings are the main problems limiting its routine usage in analytical practice. The type of sorbent used as fibre coating is the key parameter governing the recovery and selectivity of SPME [13]. Such coatings as commercially available are made from polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA), Carboxen (CAR) and polyethylene glycol (Carbowax, CW), obtainable in various thicknesses and combinations (PDMS/DVB, PDMS/CAR, CW/DVB) [33–35]. Unfortunately, these fibres have a poor affinity for polar analytes and do not always meet expectations

regarding specific applications, such as the extraction of polar analytes from polar media; this is especially apparent in the extraction of analytes from aqueous media because of the considerable affinity of water for polar analytes [36]. Table 1 lists basic information on commercially available SPME fibres and manufacturers' recommendations regarding their range of application.

The fundamental principle underlying the choice of extraction material is that polar and nonpolar sorbents respectively exhibit high affinities for polar and nonpolar analytes. According to this principle, then, only fibre coatings made from PA and PEG can be used to sample polar analytes like phenols [49,50] or alcohols, amines and ethers [44,51]. It is because of these difficulties that efforts are being made to develop techniques for producing new sorbents capable of isolating polar analytes from polar matrices. Even though the conditions for synthesizing new sorbents described in the literature are usually hard to reproduce, many reports have been published in recent years on new methods of preparing extraction fibres, the conditions of synthesis of new sorbents, and the their applications (esp. for extraction of analytes from samples with a highly complex matrix composition). Among these sorbents are: polycrystalline graphites [52] molecularly imprinted polymers [53], immunosorbents [54], polymers produced by sol–gel synthesis [55], and conducting polymers [56].

Highly specific polymer sorbents are being used as SPME fibre coatings because of the difficulties that may crop up with carbon-containing adsorbents. These materials possess active centres requiring the application of high temperatures for the desorption of less volatile compounds, which may lead to the decomposition of thermally less stable analytes. Polymeric sorbents can make use of non-specific interactions, principally dispersive ones (on their surfaces there are no functional groups or groups capable of ion exchange), and various kinds of specific interactions due to the presence of functional groups, enabling the formation of hydrogen or ionic bonds. With new technologies for the synthesis of polymeric materials, low-cost sorbents can be obtained that give high recoveries ensuring high sensitivities, and that have good mechanical strength, excellent resistance to high temperatures and to acids, bases, salts and organic solvents [57].

## 3. Properties of PEG and its application as a sorbent in extraction techniques

Polyethylene glycol (PEG) or polyethylene oxide (PEO) CAS no. 25322-68-3 is a colourless polyether polymer which, depending on its molecular mass, can exist as a thick liquid or a waxy solid. The material is simply obtained by the polymerization of ethylene oxide; therefore, no dangerous or toxic compounds are needed for the synthesis. PEG is a hygroscopic material, mixes with water in all proportions, and is also soluble in other glycols, ethanol, glycerol, chloroform and acetone. Table 2 lists the most important physicochemical properties of PEG. Since PEG is entirely biocompatible, it has been used in various kinds of *in vivo* studies [58]. It is also fairly strong mechanically and thermally resistant (even to 320 °C); it is used as an emulsifier, an additive to cosmetics, drugs and surface active substances, as a wood preservative and as a stationary phase in gas chromatography [59–64]. Instruments with columns using PEG stationary phase are highly efficient, have an excellent run-to-run and column-to-column reproducibility, and are highly selective with respect to polar analytes enabling very good separation of analytes with similar boiling points [64].

PEG is used as an SPME fibre coating under the trade name Carbowax®; these coatings are 60 μm thick and, according to the manufacturer, are intended for sampling alcohols and polar compounds with a molecular mass of 40–275 [32]. It is also the extraction phase for in-tube SPME. This latter technique was developed to facilitate the hyphenation of SPME to HPLC and to enable SPME to be automated, which would improve its reproducibility and limit its drawbacks [19,66]. In this approach the extraction phase is formed as a lining inside the SPME needle; alternatively, parts of chromatographic columns can be used for this purpose. Analytes are retained in the extractant during a number of cycles in which the sample is sucked into then ejected from the syringe; extraction can also take place after a single filling of the needle. The analytes are desorbed directly in the injector of the monitoring instrument by flushing the needle with carrier gas and directly injecting the analytes into an HPLC column [24]. In-tube SPME is frequently used to collect analytes from environmental, biological and food samples [67,68], whereas the PEG inside the capillary tubes (trade name Omegawax) is used mainly for the collection of pesticides [19], BTEX and phenols [69] from aqueous solutions as well as narcotics and β-blockers from biological samples [70,71].

**Table 2**
Physical properties of polyethylene glycol [65].

| Properties | Description |
|---|---|
| Appearance | Clear liquid or white solid |
| Odour | Mild |
| Solubility | Hydrophilic, soluble in water, methanol, benzene, dichloromethane; insoluble in diethyl ether and hexane |
| Density | 1.1–1.2 (increases as molecular weight increases) |
| Melting point | Increases as molecular weight increases: PEG1500 44–48 °C, PEG4000 54–58 °C, PEG6000 56–63 °C |
| Degradation temperature | 234 °C |
| Stability | Stable under ordinary conditions of use and storage |
| Toxicity | Non-toxic and non-immunogenic |
| Hazardous decomposition products | Carbon dioxide and carbon monoxide may form |
| Flash point | 182–287 °C |
| NFPA ratings | Health: 0, flammability: 1, reactivity: 0 |

## 4. Techniques for coating extraction fibres with a PEG film

Depending on the coating material, various ways are used to coat SPME fibres, which may affect the durability of the coating. In the case of polymeric sorbents like PEG the simplest technique is to dip the fibre in molten polymer. This method is quick and very convenient, but the coatings produced have an irregular structure and the sorbent film is not of uniform thickness.

## 5. The sol–gel technique for depositing an extraction film on the surface of an SPME fibre

An alternative means of depositing an extraction film on an SPME fibre is the sol–gel technique, and PEG coatings are also produced in this way [72,73]. Conveniently and under mild conditions, this technique enables both inorganic and hybrid organic-inorganic polymers to be obtained with a high degree of purity and homogeneity [74]. Used as SPME fibre coatings, these materials are highly selective and offer good analyte recoveries. In addition, by manipulating the composition of the reaction mixture and the conditions of the synthesis, the polymers can be given the following properties [75]:

- the desired shape,
- the desired surface properties,
- elasticity,
- considerable chemical and photochemical resistance [76,77],

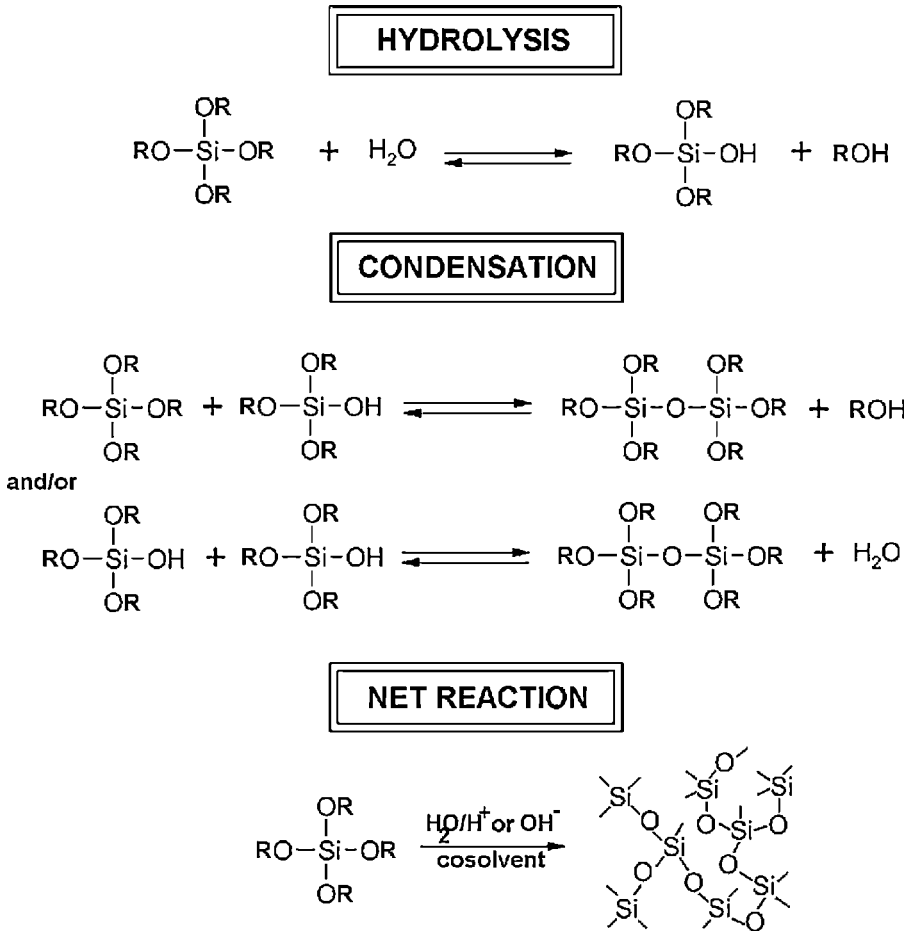


**Fig. 1.** Sol–gel synthesis of polymers.

- enhanced thermal stability [77] and stability across the whole pH range [78,79],
- substantial porosity and a large specific surface area [80].

The sol–gel synthesis of polymers is based on the hydrolysis of an organic precursor (usually a metal alkoxide $M(OR)_x$) followed by the alcoholic or aqueous condensation of the precursor [81]. During this process alkoxy groups are replaced by hydroxyl groups, and there is partial hydrolysis of the alcoholates formed. During condensation, the sol particles aggregate, the viscosity of the mixture increases due to the formation of bonds between the chains, after which the physical structure of the sol changes into a three-dimensional lattice – the rigid gel (Fig. 1). Depending on the type of catalyst used in the synthesis, one can obtain long, linear, weakly cross-linked polymers in the form of a homogeneous, thick gel with small pores (using acidic catalysts like trifluoroacetic acid) or polymers with a strongly condensed structure and a high degree of cross-linking (with basic catalysts like ammonium hydroxide or NaOH). The consequence of very rapid gelation is the presence in the structure of a large quantity of monomers, which are removed during drying, as a result of which the finished polymer has a very loose, porous structure [55,82].

SPME fibres with a sol–gel produced sorbent layer are used to sample a wide range of analytes: PCBs [83,107], phenols [84–87,94], aromatic amines [88–91,94], organometallic compounds [92], PAH [78,83], MAHs [93], BTEX and chlorobenzenes [80,94] and organophosphorus pesticides [95–97] from water [98], air, food, biological fluids and other media with a complex matrix composition [55]. Sol–gel produced polymers are also used in other SPE techniques [99–101] and as fillers in capillary columns for GC [102] and HPLC [103].

Sol–gel is also used for preparing extraction fibres with a PEG film. In SPME, such fibres have a shorter extraction time, large porosity and give better analyte recoveries than the extraction fibres currently available on the market [72]. The first literature report on the sol–gel production of extraction fibres with a PEG film described the synthesis and application of a PEG extraction coating with an average molecular mass of $4 \times 10^6$ g mol$^{-1}$, available under the trade name Superox-4 [104]. This material is stable at high temperatures, is highly porous and adheres well to all types of glass [105]. It is more usual, however, to produce PEG-coated extraction fibres with small molecular masses, between 14 000 and 16 000 g mol$^{-1}$ (trade name Carbowax 20M), since it is more porous than Superox-4 [104]; also, its properties are far better known. Low-molecular-mass PEG is far more polar than its high-molecular-mass counterpart and so is better suited to the extraction of the more polar organic compounds containing hydroxyl, carboxyl or amino groups, which are the main contaminants of the environment [73]. Carbowax M20 has a high minimal operating temperature (ca 70 °C), but it is much less resistant than Superox-4 to high temperatures [106].

Extraction times with sol–gel produced PEG materials are very short, thanks to their large surface area and porosity, which improve analyte transport [104]. With such materials BTEX compounds have been sampled in less than 10 min and desorbed in the column injector in barely 20s [72]; this is possible because the sol–gel technique produces very thin sorbent films, which in turn means that the system reaches equilibrium very quickly [107]. Sol–gel produced PEG films are used to sample BTEX compounds

[72,104,108], phenols [104], aldehydes, ketones, aromatic amines and alcohols [73], as well as drugs, narcotics and their metabolites [109,110]. Where these films were used to extract drugs, the samples were taken *in vivo*, so the fact that they are biocompatible is very important. Moreover, they guarantee a high sensitivity and accuracy of analysis as well as a short extraction time, despite the complex composition of the matrix (blood). This particular SPME arrangement is thus suitable for determining polar analytes *in vivo* [109].

## 6. Electrochemical techniques for depositing sorbent films on SPME fibres

Sorbent films can also be deposited on SPME fibres electrochemically in that a metal SPME fibre is coated with a suitable conducting polymer, usually by cyclic voltammetry (CV) or potentiometry. The advantages of these methods are that:

- they are relatively cheap,
- any fibre can be coated, even one with an irregular or porous surface,
- the coating is homogeneous and pure,
- the polymer coating can be obtained in oxidized or reduced form,
- the deposition time on the fibre is very short [111].

The fact that the SPME fibre is of metal gives it good mechanical strength [112]. With electrochemical techniques, a platinum fibre can be coated with extraction films of poly(3-dodecylthiophene) (P3DDT) [113,114], polypyrrole (PPy) and its derivatives [115–118] and polyaniline (PANI). Such fibres are used to sample phenolic compounds, PAHs [119] and also polar and nonpolar aromatic compounds and alcohols [115]. The same techniques are used to produce metal coatings, for example, a thin layer of gold for extracting mercury [120], of lead oxide for sampling BTEX [121], or of copper chloride in the determination of amines [122].

These techniques are also applied to produce PEG films with which to coat fibres made from the biocompatible alloy Nitinol, itself coated with a layer of zirconium oxide [123,124]. This alloy is highly elastic, resistant to stretching and corrosion; SPME fibres made from this material are therefore very strong [125,126]. PEG is also deposited on porous zinc coated silver fibres: the resulting extraction fibres have excellent resistance to high temperatures and corrosion and are very good electrical conductors [127].

## 7. Membrane solid-phase microextraction (M-SPME) – a novel means of depositing PEG films on extraction fibres

Despite the many different technical approaches to SPME, many aspects of the extraction of polar analytes from samples containing polar matrix components still require improvement, and the problems causing lowered recoveries need to be eliminated. In order to solve the problem of the poor affinity of extraction coatings for polar organic compounds, highly polar sorbents ought to be used as the extraction phase; but competitive adsorption processes could occur during the extraction of polar analytes from polar media, leading to the analyte being leached out of the extraction coating. Very few fibres for extracting polar analytes are commercially available, and all of them have a relatively low affinity for polar compounds. Moreover, during the extraction of analytes from highly polar media, the extraction coating may partially dissolve in the sample.

One way of overcoming these difficulties in SPME could be to use a highly polar extraction phase of PEG, but to keep it separate from the analysed sample by depositing a nonpolar membrane made from a hydrophobic sorbent material on the PEG coating

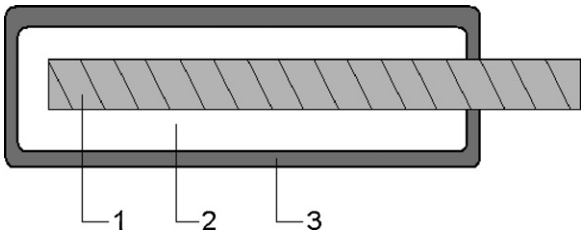


**Fig. 2.** Construction of an extraction fibre with a double-layer sorption system: (1) glass fibre, (2) PEG coating, (3) PDMS coating.

(membrane solid-phase microextraction M-SPME) [128]. In this system analytes migrate from the sample matrix across the hydrophobic, thermally stable membrane (made from PDMS) to be retained on the polar solid-phase made from highly polar PEG [128]. Both sorbent layers are deposited on the SPME glass fibre by immersing this in the molten polymer. This double-layer sorption system for SPME is illustrated in Fig. 2.

This double-layer PEG/PDMS sorption system has good mechanical properties and is thermally very stable: a thermal resistance test, in which the fibre was heated in a nitrogen atmosphere to 220 °C, showed that the extraction coating did contract very slightly, but that the loss of mass was minimal. This is because PDMS is thermally stable up to ca 300 °C, thus enabling the thermal desorption of analytes absorbed on the fibre [128,129]. The fibres

**Table 3**
Comparison of the properties of a double-layer PEG/PDMS sorption system with commercially available SPME fibre coatings.

| Commercially available fibre coatings | Double-layer PEG/PDMS fibre coatings |
|---|---|
| • Choice of commercially available fibre coatings is limited | • Choice of membrane materials limited to the two commercially available ones, i.e. PDMS and PA |
| • High cost | • Low cost |
| • Poor selectivity | • High selectivity |
| • Low chemical resistance | • Low mechanical stability |
| • High thermal stability | • High thermal stability |
| • Coatings have an regular structure and the sorbent film is of uniform thickness | • Coatings have an irregular structure and the sorbent film is not of uniform thickness |
| • They may have active centres, which means that high temperatures are needed to desorb the less volatile compounds | • Do not possess active centres, so desorption of analytes at moderate temperatures is possible |
| • The in-house production of fibres is quite complicated: the conditions of synthesis are difficult to reproduce as they depend on a great many factors. | • Synthesis by immersing the core in a solution of molten polymer is a quick and very convenient method |
| • Coatings available in different forms and sizes and in combinations of polar/nonpolar sorbents like PDMS/DVB, PDMS/CAR or CW/DVB | • Double-layer fibre coatings enable highly polar sorbents to be used without the risk of their dissolving in the sample matrix |
| • Different extraction and desorption times | • Short extraction and desorption time |
| • Carboxen gives the PDMS/CAR coating a greater specific surface area, as a result of which extraction of VOC analytes is very efficient | • Experiments using the PEG/PDMS system on a standard mixture of phenols have given a tenfold better recovery than commercially available PA coatings |
| • Do not meet expectations in specific applications; limited applicability in the extraction of polar analytes from samples with a polar matrix composition | • Applicable in the extraction of polar analytes from samples with a polar matrix composition. |

used in M-SPME were not damaged by water either, nor was any water sorbed or polar solid-phase lost, thanks to the presence of the hydrophobic, nonpolar membrane. The double layer sorption system thus allows highly polar sorbents to be used as extractants without the risk of their dissolving in the polar sample matrix. It is also significant that PDMS and PEG (for small molecular masses) at extraction temperatures are pseudoliquids; analyte retention is thus due to absorption, that is, dissolution in the extractant. This means of retaining analytes eliminates the risk of incomplete desorption or the decomposition of compounds with a low degradation temperature since the analytes are not strongly bound to the absorbent; desorption can therefore be carried out at low temperatures. In addition, retaining analytes by having them dissolve in the stationary phase eliminates problems like artefact formation or the displacement of analytes from active sites by matrix components. Finally, PDMS and PEG are universally applied as stationary phases in GC: they are therefore easily identified by mass spectrometry since their decomposition products are known [128].

The times of extraction and desorption of analytes using PEG/PDMS fibres are short (a few minutes). Additionally, tests of this sorption system in SPME sampling of phenols from standard solutions, indicated recoveries 10 times greater than with commercially available polyacrylate coatings for the same desorption times [128]. Preliminary studies on the use of this system to sample VOCs from standard aqueous solutions using SPME showed a high extraction recovery from the headspace of the most polar compounds in the mixture. The recoveries obtainable with PEG/PDMS fibres and with headspace extraction are comparable or better than the recoveries of such compounds using commercially available PDMS/DVB/CAR coatings (recommended by Supelco for extraction of this class of compounds). The use of a highly polar sorbent in M-SPME and the benefits of the double-layer sorption system make it possible to completely overcome the problems with sampling polar analytes from polar matrices. Table 3 compares the properties of a double-layer PEG/PDMS sorption system with commercially available SPME fibre coatings.

## 8. Summary

In view of the challenges that contemporary analytical techniques must face up to, 'green' solvent-free sample preparation methods like SPME are becoming ever more important. Developments in the production of new fibre coatings for this technique are aimed at increasing the amounts of polar analytes extracted from matrices containing polar components. New technologies are becoming available for the simple and inexpensive synthesis of extraction fibres from highly polar polyethylene glycol (PEG). Such fibres are very stable at high temperatures, are mechanically strong, offer very short extraction and desorption times, and exhibit excellent affinity for polar analytes. With PEG films large quantities of polar analytes can be sampled with good selectivity, rendering the SPME technique highly sensitive.

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