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REVIEW

Solventless sample preparation techniques based on solid- and vapour-phase extraction

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Abstract The main objective of this review is to critically evaluate recent developments in solventless sample preparation techniques. The potential of a variety of sample preparation techniques based on solid- and vapour-phase extraction techniques is evaluated. Direct thermal extraction and derivatization processes to facilitate the extraction of analytes in different areas are included. The applicability, disadvantages and advantages of each sample preparation technique for the determination of environmental contaminants in different matrices are discussed.

Keywords Sample preparation · Thermal desorption · Gas chromatography · Extraction techniques · Environmental contaminants

Introduction

Choosing an appropriate sampling (preparation) technique that provides representative samples of analytes plays a key role in accurate and reliable assessment of the content and the concentration of volatile and semivolatile organic compounds present in various environmental components and products resulting from the generation of human labour. The sample taken should reflect the actual state of the object. Therefore, the selected sampling (preparation) technique should be characterized by such features as:

- Being easy to conduct activities and operations in situ
- Possibility of determining the analytes in the medium in a given range of concentrations with the required precision and accuracy
- Low unit cost (so that research can be conducted on a large scale)

However, other aspects concerning operator safety and the environmental impact of analytical methods should be considered. For example, during the 1990s, side effects of analytical methodologies developed to analyse different kinds of samples (including environmental samples that generate a large amount of chemical waste) resulted in a great environmental and human impact. In some cases, chemicals employed for analysis were even more toxic than the substances being determined. Taking into account current public concern with environmental matters, environmental analytical studies and the consequent use of toxic reagents and solvents have increased to a point at which they have become unsuitable for continued usage without an environmentally friendly perspective [1].

In recent years there has been rapid growth of interest in subjects related to clean analytical chemistry or environmentally friendly analytical methods, including solventless sample preparation techniques. The scientific references found in the Science Citation Index (SCI) database relating to green analytical chemistry (GAC) [2] and the literature on this topic have grown since the 1990s. This change in the rate of publications on GAC methods is related to the increasing concern of the scientific community about the environmental impact of their actions [1]. Strong interest in this approach is associated with both ecotoxicological and economic aspects. As a result of the application of solventless sample preparation techniques for primary laboratory practice, the emission of toxic solvents into the environment is avoided—as is the use of high purity solvents, which are expensive [3].

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In this paper, state of the art solventless sample preparation techniques based on solid- and vapour-phase extraction are reviewed. Direct extraction methods of analytes in different areas are included.

Sorptive extraction techniques

Sorptive extraction techniques are based on the distribution equilibria between the sample matrix and sorptive materials. Analytes are extracted from the matrix into the non-miscible extracting phase. In contrast to adsorption techniques (e.g. solid-phase extraction, SPE), where the analytes are bound to active sites on the surface of the adsorbent materials, the total volume of the extraction phase is important. Sorptive materials (or sorbents) are a group of polymeric materials with a glass transition temperature (T_g) below the temperature at which the material is used during the sampling, storage and desorption processes. At temperatures above their T_g, polymeric materials no longer behave as solid materials but assume a gum-like, or even liquid-like, state with properties similar to those of organic solvents (e.g. diffusion and distribution constants). Sorbents are, in principle, homogeneous, non-porous materials in which analytes can actually dissolve. The analytes do not, therefore, undergo real (temporary) bonding with the material but are retained by dissolution. Extraction of analytes depends on the partitioning coefficient of solutes between the phases. The octanol–water distribution coefficient ($K_{o/w}$) can be used as an indication of how well a given analyte will be extracted [4].

Four sorptive extraction techniques can be distinguished. The first, open-tubular trapping (OTT), is the oldest technique and employs a (thick film) capillary gas chromatography (GC) column for sampling. The second technique, solid-phase microextraction (SPME), is based on the use of a polydimethylsiloxane (PDMS)-coated fibre which, when not in use, is protected by being withdrawn into the needle of a syringe-like device. The third technique is stir bar sorptive extraction (SBSE) which is based on the static extraction of liquid samples with a sorbent-coated stir bar [5]. The fourth sorptive technique, gum-phase extraction (GPE), is based on a bed packed with sorbent material. In this contribution, the state of the art in sorptive sampling and thermal desorption is reviewed.

Open-tubular trapping (OTT)

A capillary microextraction technique which employed an open-tubular fused silica capillary column as an extraction device was first developed in 1986 as open-tubular trapping (OTT) [6]. In OTT, ambient air, solution, or solution headspace is sampled by passing a gas or liquid through the open capillary. In OTT, sorption is carried out as an equilibrium process and the amount of analyte retained by the stationary phase and the equilibrium is directly related to its concentration in the sample solution. The analytes are desorbed either with a small amount of solvent or by thermal desorption and are usually used in combination with GC. The sample is forced to flow through the capillary and analytes reach the trapping medium, coated onto the walls, by diffusion. The thermal stability of GC stationary phases allows the collected analytes to be thermally desorbed from a trap after sampling. These analytes can be desorbed directly onto a GC column for analysis, avoiding dilution of the sample with a solvent. Sample cross-contamination and possible degradation are minimized because intermediate sample handling steps are eliminated. A schematic illustration of OTT sampling is presented in Fig. 1 [7]. Open-tubular traps have been successfully employed for a range of gaseous samples [8, 9], plant volatiles [10–12] and environmental air samples [13]. Dudek at al. [14] used a piece of a commercial capillary GC column coated with PDMS in OTT for the sampling and enrichment of select volatile non-polar organic compounds from a workplace atmosphere (a woodworking shop). Results obtained by means of OTT confirm that this method is suitable for sampling organic pollutants from air.

Open-tubular trapping can be an attractive alternative to traditional techniques for the enrichment of aqueous samples [5, 15]. Several OTT approaches, involving off-line [16] or on-line [17, 18] coupled with GC, have been described.

Solid-phase microextraction (SPME)

SPME was introduced by Pawliszyn in the early 1990s [19]. It is a solvent-free sample preparation technique that uses a fused silica fibre coated with an appropriate stationary phase attached to a modified microsyringe (Fig. 2) [20, 21]. In SPME, partitioning of analytes between the stationary phase on a fibre and the sample takes place until equilibrium is achieved. Maximum sensitivity is obtained at the equilibrium point; however, it is not necessary to reach this point and the extractions can instead be performed for a defined period of time [22]. The extraction temperature, time and sample agitation must be optimized for each application and operating conditions must be consistent [23]. SPME can be applied to different types of samples, using two different approaches. For relatively pure liquids, extraction is performed by dipping the SPME fibre directly into the sample. For solid matrices and wastewater samples, headspace (HS) SPME is preferred, because it results in faster equilibration and higher selectivity [20]. After the coated fibre has been exposed to the sample for a given period, it is inserted into the injection port of a GC system in order to realize the analyte. In GC, this is achieved by thermal desorption, whereas in

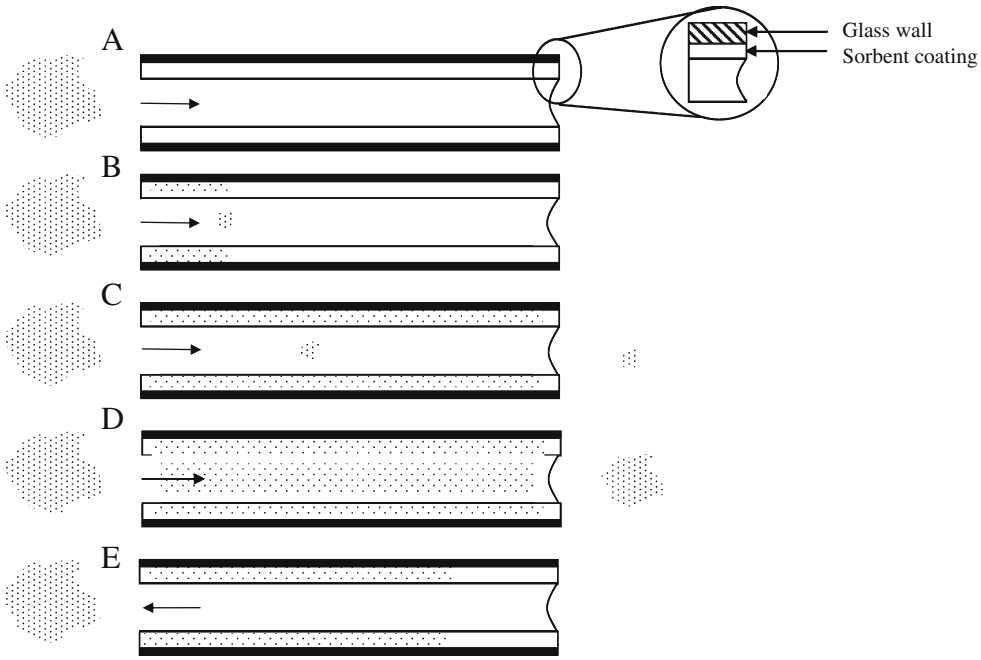

Fig. 1 Schematic illustration of OTT sampling. *A* sampling is started; *B* analytes are sorbed into the coating; *C* analytes start to break through; *D* the sorbent is in equilibrium with the sample; *E* the trap is desorbed in backflush mode

HPLC it is accomplished by dissolution and further injection with the elution solvent [24, 25].

SPME has several advantages compared to other extraction methods. It gives quantifiable results from very low concentrations of analytes and avoids the losses that can occur during extraction, concentration and clean-up steps in traditional sample procedures [26]. On the other hand, one of the main drawbacks of this technique is its limited range of stationary phases which are commercially available, only roughly covering the scale of polarity. Some of the commercially available fibres and their applications are presented in Table 1.

Recent trends in SPME are focused on solving these problems by:

- Studying new coatings with higher extraction efficiencies, selectivity and stability [28, 29]
- Development of new devices to improve the extraction process [30]
- Studying novel calibration processes [31, 32]
- Development of derivatization strategies [33, 34]

In order to effectively couple the extraction efficiency of SPME with the detection capability of ion mobility

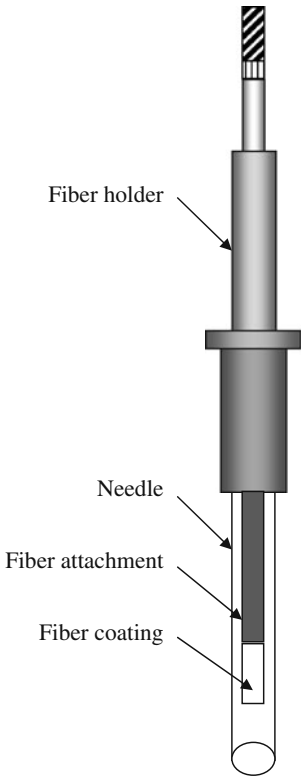

Fig. 2 Schematic diagram of SPME

Table 1 Recommended application fields for different SPME fibres [27]

Fibre	Application
PDMS 100 μm	Volatiles
PDMS 30 μm	Non-polar semivolatiles
PDMS 7 μm	Non-polar high molecular weight compounds
PA	Polar and semivolatiles
PDMS/DVB	Volatiles, amines and nitroaromatic compounds
Carbovax/DVB	Alcohols and polar compounds
Carboxen/PDMS	Gases and low molecular weight compounds
DVB/Carboxen/PDMS	Volatile and semivolatile flavourings and odorants

PDMS polydimethylsiloxane, *PA* polyacrylate, *DVB* divinylbenzene

spectrometry (IMS), Liu et al. [35] developed a new prototype SPME-IMS system as a robust, simple, rapid, energy-saving fieldable approach for on-site analysis of analytes in various matrices.

Meanwhile, SMPE has routinely been used in combination with GC and GC-MS and successfully applied to a wide variety of compounds, especially for the extraction of volatile and semivolatile organic compounds from environmental, biological and food samples.

In-needle solid-phase microextraction techniques (in-needle SPME)

In-needle extraction techniques were developed to overcome fibre-related drawbacks such as fragility, low sorption capacity, and bleeding from thick-film coatings. For this purpose, the extraction phase is fixed inside a needle instead of the surface of the SPME fibre [26]. The main advantage of this resolution is that it overcomes the mechanical stability problems of fibre SPME.

In-needle extraction techniques can be divided into methods with:

- Extraction coatings (which use a coating as an internal extraction phase immobilized in the needle)
- Extraction fillings (which use a sorbent packing material as an extraction phase)

Independent of the type of extraction materials, in-needle extraction techniques can be used in two modes:

- Static mode (in which analytes are transferred by diffusion through needles)
- Dynamic mode (in which analytes are transferred actively by pumping or under the gravitational flow of the sample phase through needles)

Inside needle capillary adsorption trap (INCAT) and needle trap devices (NTDs)

In 1997, McComb et al. designed a novel method of solventless extraction based on a combination of the SPME and purge and trap (PT) methods. In this technique, a hollow needle with either a short length of GC capillary column placed inside it, or an internal coating of carbon, is used as the preconcentration device. This approach is called inside needle capillary adsorption trap (INCAT) for the analysis of benzene, toluene, ethylbenzene and xylenes (BTEX) in air [36]. Sampling may be performed in ambient air, on the solution, or the solution headspace, by passing gas or liquid through the device, either actively with a syringe, or passively via diffusion. The trapped analytes are recovered by using direct thermal desorption, by placing the needle into the heated GC injection port [37].

The main advantages of the INCAT device lie in the simple methodology and easiness and rapidity of the analyses. Compared to SPME, the in-needle sampling device has been recognized as a robust and efficient sample preparation method [38]. The drawbacks involve the fact that the collected samples cannot be particularly large, and the desorption temperature is limited by that of the gas chromatographic injection port [38].

To enable high efficiency and repeatability of adsorption and desorption of trace quantities of BTEX from a water matrix, Kubinec et al. developed the INCAT device. A new arrangement of the fully internal volume needle capillary adsorption trap device, with Porapak Q as a sorbent material and wet alumina as a source of desorptive water vapour flow, was used for the analysis of BTEX in drinking and waste water samples [39]. To counter the disadvantages of the INCAT method, a new on-column injection system facilitating the use of large diameter INCAT devices was developed by Hrivňák et al. [40].

An in-needle trap device was also developed by Wang et al. for analysis of volatile organic compounds (VOCs) in gaseous samples [41]. Construction of this simple and integrated sampling/extraction/sample introduction device was optimized. A novel in-needle extraction device was also developed by Saito et al. [42] for the analysis of several organic solvents commonly used in a typical chemical laboratory. The specially designed needle was packed with porous beads made from polymeric material that showed excellent performance for the extraction and a suitable thermal stability for typical analysis in GC. In 2008, a needle trap device with Carbopack X as a sorbent material for sampling, preconcentration and injection of BTEX into gas chromatograph was developed by Jurdáková et al. [43]. A schematic diagram of a needle trap extraction (NTE) device is shown in Fig. 3 [21].

Solid-phase dynamic extraction (SPDE)

Solid-phase dynamic extraction (SPDE), also known as “the magic needle”, is a further development of SPME. It was first described by Lipinski [44] for the analysis of pesticides in water samples. SPDE works on the same principle as SPME, but it is a dynamic process where the headspace of the sample is repeatedly pumped through a hollow needle attached to a gas-tight syringe. The extraction phase (e.g. PDMS/Carboxen) is on the inside of the needle, as opposed to SPME where it is on the outside of a fibre. Also, the needle is much longer than an SPME fibre. The advantage of SPDE over SPME is the increased volume of sorption material. Therefore, sensitivity is better and competition effects, which may be an issue with SPME, are largely eliminated. Desorption is carried out directly in the GC injector, similar to SPME [45]. A schematic diagram of SPDE is shown in Fig. 4 [21].

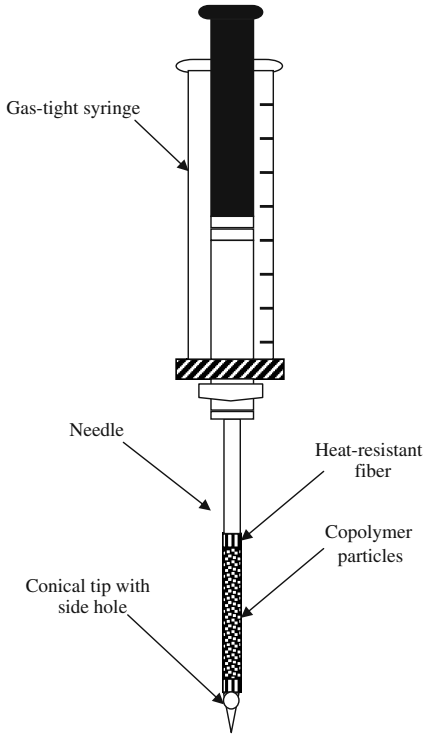

Fig. 3 Schematic diagram of an NTE device

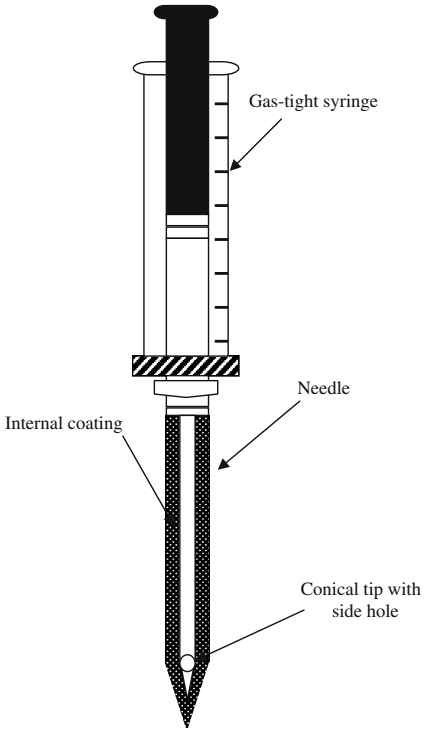

Fig. 4 Schematic diagram of SPDE

There is a fully automated commercially available system for the analysis of liquid called in-solution solid-phase dynamic extraction (IS-SPDE) [46].

Stir bar sorptive extraction (SBSE)

Another solid-phase alternative to using organic solvents is stir bar sorptive extraction (SBSE), which is based on the interaction of analytes with a coating of PDMS deposited on a glass stirrer bar (Twister). It was introduced in 1999 by Baltussen et al. to overcome the limited extraction capacity of SMPE fibres [47, 48].

Stir bar sorptive extraction applies stir bars, varying in length from 1 to 4 cm, coated with a relatively thick layer of PDMS (0.3–1 mm). Using a thicker polymeric layer than that employed in SPME results in a high enrichment factor. Sampling is performed until breakthrough or, for even higher sensitivity, until all analytes are in equilibrium with the sorbent. This technique can be applied for gaseous and liquid samples, although for the latter drying is required, which induces a loss of volatile compounds [49].

The applicability of SBSE can be evaluated by using the octanol–water distribution coefficient ($K_{o/w}$) as an indicator of how well, if at all, a given solute can be extracted with SBSE [50]. Sandra [51] reported that a high enrichment factor could be achieved for analytes even with octanol–water distribution coefficients higher than 100 ($\log K_{o/w} > 5$). Typically, solutes should have relatively high $\log K_{o/w}$ values for SPME (less than ca. 3).

After a certain stirring time, the stir bar can be desorbed with a small volume of a suitable solvent, but for volatile and semivolatile compounds, on-line thermal desorption provides an approach that avoids using organic solvents.

Currently only PDMS coating is commercially available, making the technique most suited to non-polar analytes from aqueous media. However, this technique can be used for more polar compounds by using derivatization. To improve the recovery of more polar analytes, a “dual-phase twister”, which combines both absorption and adsorption, has been described for SBSE [52]. A schematic diagram of a dual-phase stir bar for SBSE is shown in Fig. 5 [53].

The large amount of sorbent causes some problems. The extraction time is longer, as it takes more time to reach

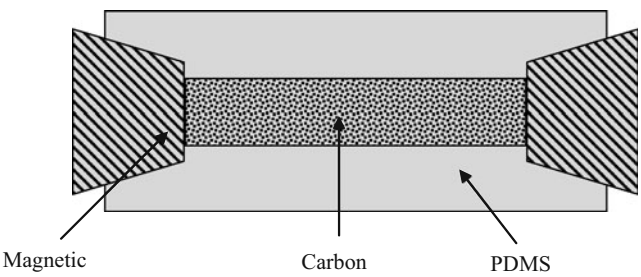

Fig. 5 Schematic diagram of a dual-phase stir bar for SBSE

equilibrium. Moreover, desorption takes more time and it may be necessary to reconcentrate the sample band by using cold-trapping during the transfer. The clear benefit of SBSE over SPME is better sensitivity, because the absolute amount of analytes transferred into the chromatographic system is higher. In addition, SBSE can also be used for extraction of relatively polar analytes [54, 55].

Popp et al. [56, 57] employed silicone materials (in the form of rods and tubes) for enrichment of organic compounds, similar to the commercialized Twister. These materials are inexpensive, flexible and very robust, and have successfully been applied for direct extraction of semivolatile compounds in water [58].

Gum-phase extraction (GPE)

Gum-phase extraction (GPE) is another technique that employs polymeric sorbents (e.g. PDMS) filled as a bed in a column, most commonly in the form of particles (typically 300 μl). This technique, which resembles SPE, was first reported by Baltussen et al. in 1997 [48, 59].In principle, GPE can be used for both liquid and gaseous samples. Dynamic sampling has been employed with both gaseous and liquid (aqueous) samples, but the usefulness of the GPE technique for the enrichment of trace compounds from water is limited since the packed tube needs to be dried prior to desorption. For gaseous samples, GPE has the same advantages as OTT and SPME in terms of inertness and thermal desorption characteristics [60].

In GPE, the analytes are dynamically trapped on the sorptive preconcentration trap, an approach called breakthrough sampling. In breakthrough sampling, the analytes will be retained in the packed bed and, consequently, the concentration of analyte in the sample will decrease through the bed. Initially the analyte concentration in the outgoing sample phase will be zero and sampling is usually stopped when the first analyte of interest starts to elute from the trap. Desorption of the trapped analytes can be performed with liquid or by heating (the thermal desorption approach is preferred, because it ensures higher sensitivity).

The performance of a cartridge filled with 100% PDMS particles was compared to the performance of adsorbents like Tenax TA and Carbotrap 300 for the sampling of volatile analytes by Baltussen et al. [61]. Dynamic sampling on PDMS and Tenax was examined for sampling of the volatile solutes emitted by living plants [62].

Equilibrium gum-phase extraction (EGPE)

A new concept for sorptive sample enrichment is that of equilibrium gum-phase extraction (EGPE). This technique is very similar to GPE, but instead of employing breakthrough sampling, the PDMS sorbent in EGPE is completely saturated to equilibrium so that the maximum amount of all analytes is sorbed [63]. Because of the nature of the sorption mechanism (basically dissolution) all analytes partition independently into the sorbent and displacement effects do not occur. This is an advantage over adsorption materials. Additionally, this theory allows for the calculation of enrichment factors from literature retention index data [64]. EGPE can be applied to aqueous and gaseous samples. It has proven to be very successful for the enrichment of volatile compounds [60].

Closed-loop stripping analysis (CLSA)

Closed-loop stripping analysis (CLSA) is a quantitative method used for extraction and detection of VOCs in water. It was introduced in 1973 by Grob [65]. A new technique for isolating analytes from the water to the gas phase involves eluting analytes from the water with a continuous stream of inert gas which is then directed to a bed of solid sorbent, where the compounds are trapped. After removal of analytes the inert gas is recycled back into the vessel with aqueous sample and purges the next batch of analytes on solid sorbent. The analytes are released from the sorbent by elution with a solvent or by thermal desorption [66].

Closed-loop stripping analysis is routinely used to monitor the quality of river water for a broad range of volatile compounds [67]. However, lower volatility compounds are not likely to be analysed with CLSA, which can severely limit its application. Moderately and highly polar ionizable organics are poorly purged or not recovered [68].

Sorption tubes

In sorbent-based methods, such as sorption tubes, analytes are extracted from air by adsorption onto the sorbent surface. The sampling of analytes from the gas phase into the sorption tube might occur using the dynamic or passive methods [69].

In the case of the active sampling method, air is passed through tubes packed with appropriate sorbents. Air flow through the trap is forced by the appropriate mechanical devices (i.e. aspirators) or pumps [70]. Unlike active sampling techniques, passive sampling techniques do not require forced air flow through the bed of sorbent. In this case, the movement of molecules is effected by diffusion according to Fick's first law and, therefore, no additional devices for collecting air samples or measuring their volume are necessary [71].

For any type of sampling exercise, it is possible to make a choice of the type of sorbent, the method of sampling (pumped or diffusive), the method of liberation of trapped analyte (solvent or thermal extraction) and the method of analysis. Typically, the same sorbents are used in diffusive

samplers as in pumped sorbent tubes. On the other hand, the most common sorbents used for sampling with solvent desorption are only rarely encountered where thermal desorption is required. This is because their high surface activity can lead to sample degradation at the high temperatures required for desorption [72].

The tubes used to hold the sorbent for thermal desorption are made of stainless steel or precision-bore borosilicate glass, with precise dimensions to ensure a leak-free connection to the desorption units [73].

A wide variety of organic and inorganic sorbents are available for collection of ambient VOCs [74, 75]. Selection of suitable adsorbents is very critical as it depends on the sample matrix and on the compound to be collected. A useful review of sorbents for thermal desorption has been published [76, 77].

There are some criteria that should be taken into account during the selection of sorbents:

- Breakthrough of the analytes has to be avoided [78]
- Contamination of sorbents must be avoided before and after sampling
- High adsorption capacity in relation to the fortified analytes
- Hydrophobic nature of the sorbent to reduce to a minimum the process of simultaneous adsorption of water vapour
- High thermal stability, such that thermal desorption can be performed at sufficiently high temperature
- Affinity for a particular group of compounds, allowing a degree of selectivity for enrichment.

The arrangement of the sorbents is such that the least volatile compounds are trapped on the weakest sorbent at the front end of the tube, and successively more volatile compounds are trapped by increasingly strong sorbents further down the tube. Desorption then takes place in the reverse direction, as with single-bed tubes. A schematic diagram of a multi-sorbent tube for dynamic sampling of VOCs is shown in Fig. 6 [79].

In the literature, many papers can be found describing different thermal desorption (TD) coupled to GC-MS methods development for a wide range of VOCs analysis [80, 81].

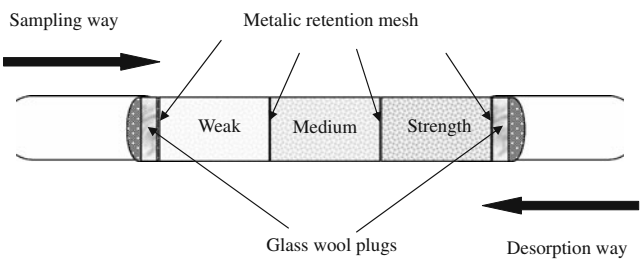

Fig. 6 Multi-sorbent tube for dynamic sampling of VOCs

Sorbent tubes have formed the basis of the US Government's agency methods (NIOSH 2549, EPA TO-17) [82, 83].

Hryniuk et al. [84] demonstrated the potential of using a combination of TD tubes and selected ion flow tube mass spectrometry (SIFT-MS) for breath analysis, an approach that may find utility in a clinical setting which does not allow on-line analysis of breath.

Field air sampling with sorbent tubes and multidimensional GC-MS/olfactometry for simultaneous chemical and sensory analysis of livestock odorants was used to develop an odour characterization method for specific livestock odorants and develop a quantitative method for the key odorous compounds responsible for livestock odour emissions [85].

Vapour-phase extraction

The first application that mentioned the concept of headspace (HS) sampling was the "aerometric method" for rapid determination of alcohol in water and bodily fluids [86]. The terms "headspace" and "headspace analysis" were first used in 1960 by Stahl et al. [87], while the first communication in which HS sampling was combined with GC analysis was by Bovijn et al. [88].

A common feature of headspace analysis methods is the use of partition law which states that, at given conditions of pressure and temperature, the ratio of the component concentrations in the liquid phase (L) and gas phase (G) at thermodynamic equilibrium is constant. This ratio is called partition coefficient [89]. Headspace analysis as a method of preparing samples for proper analysis (performed by any method) involves the transfer of the analytes from the original sample—condensed matter, mostly liquid—to the gas phase, which is to be analysed. Therefore, with the analytical procedure, combining HS with an appropriate separation technique, it is possible to obtain information on the composition of the original sample (liquid or solid) based on analysis of the gas phase remaining in equilibrium with it. Traditionally HS sampling operates either in static (S-HS) or dynamic mode (D-HS).

Static headspace (S-HS)

Static headspace (S-HS) procedures for the analysis of VOCs in aqueous or other matrices have been used extensively as a means of determining analytes without interferences from the sample matrix. In S-HS, which relies on volatilization to separate analytes from a sample matrix, important factors are related to diffusion and surface area. For accurate quantitative analysis, the temperature/pressure conditions of a sample vessel are critical. In this resolution, the headspace is sampled directly with a microsyringe or by filling a loop. Such determinations require large Henry's

law constants and therefore are applicable to volatile compounds [90].

The S-HS method eliminates many steps of error-prone and time-consuming manual sample preparation procedures and allows for the introduction of a gaseous sample into an analysis system. On the other hand, the most significant drawback of S-HS is its lack of sensitivity. Generation of a gaseous sample is an equilibrium process that limits the amounts of a specific analyte available for analysis within the practical restraints of time and temperature. Additionally, the injection size is a bottleneck since most GC systems can handle injections of only a few cubic centimetres [91].

Headspace analysis could run under equilibrium or non-equilibrium conditions. The latter may be carried out in two cases [92] when:

- The time needed for equilibration is too long for the intended purpose, control or for routine measurements
- The sample is heat sensitive, and it might be damaged in the course of full equilibration.

Dynamic headspace (D-HS)

One of the first applications of dynamic headspace (D-HS) was due to Herout, who collected the volatile fractions of *Viol odorata*, *Lycaste macrobulbum* and *Hyacinthus orientalis* through an Apiezon trap [93].

The dynamic headspace method is a solventless, highly reproducible, automated extraction procedure for volatiles from almost any matrix for quantitative and qualitative determinations, which extends the headspace method and uses concentrator technology to achieve far more sensitive detection limits. In the dynamic headspace technique, the equilibrium between the phases is continually altered. D-HS is generally based on two main approaches:

- The purge and trap (PT) approach, which is based on bubbling through the sample (liquid or solid) with an inert gas (usually helium or nitrogen). The volatile fraction is accumulated from the gaseous flow stream stripped through the matrix onto a trapping medium: cold trap, a sorbent, an adsorbent or specific reagent or sorbent for a given class of compounds [94]. This step can be carried out in an open or closed loop [95]. In the open-loop configuration, the non-trapped molecules are eliminated. In the closed-loop method, the gaseous phase flows through the sample and the trap in a closed circuit [96].
- The dynamic approach, where analytes are sampled from the gaseous flow stream passed over the sample [97].

The sampled volatiles are generally recovered either by solvent elution or (more often) by thermal desorption on-line or off-line to the GC.

One of the main problems of dynamic headspace is the adsorption of water on the trap. Water can be a major source of trouble if the sample contains it in high amounts (beverage, aqueous sample, foods). In the case of adsorption of the analytes onto a solid sorbent, a certain percentage of water will also be retained. Water subsequently released during desorption may clog up the cold trap or the cryofocusing trap at the head of the column. Therefore, efforts have been made to develop a sorbent with low water affinity. But even in the case of the hydrophobic sorbents, the trapping of water can cause problems when the relative humidity of the sample is above 90% [98]. Too much water entering the system can also damage the MS detector [99] and induce a modification of the spectrum, rendering identification difficult [100]. Therefore it may be necessary to introduce some solutions to avoid the presence of water in the analytical system (Table 2).

Massolo et al. [108] described the optimization of the main instrumental parameters of a home-made purge and trap GC system for the simultaneous determination of chlorofluorocarbons (CFCs) in seawater samples. In order to concentrate high volumes of water for trace analyses and stable carbon isotope measurements of volatile halogenated organic compounds in seawater a purge and trap continuous flow system was developed [109].

High concentration capacity headspace techniques (HCC-HS)

Interest in HS technique concurred with the introduction of an additional approach: high concentration capacity headspace techniques (HCC-HS). HCC-HS techniques are based on either the static or dynamic accumulation of volatile(s) on polymers operating in sorption and/or adsorption modes, or more seldom, on solvents [97]. HCC-HS techniques are as simple, fast, easy to automate, and reliable as S-HS, and they show analyte concentration factors comparable to those of D-HS [110].

Headspace solid-phase microextraction (HS-SPME)

The first HCC-HS technique to appear was HS-SPME, introduced by Zhang and Pawliszyn in 1993 as an extension of SPME [111]. They advanced a theory for SPME applied to HS sampling [112] and showed that analyte recovery from headspace by fibre depends on two closely related but distinct equilibria: the matrix/headspace equilibrium and the headspace/polymeric fibre coating equilibrium. HS-SPME has been shown to be a successful bridge between static (S-HS) and dynamic (D-HS) headspace being as simple, reproducible and easy to automate as S-HS, and as sensitive and as selective as D-HS.

Table 2 Examples of solutions avoiding the presence of water in the analytical system [101–107]

Type of resolution	Description of resolution
Dry purge	Immediately before desorption, the solid trap can be flushed with an inert dry gas (helium) to remove part of the water. A part of the highly volatile compounds will inevitably be lost. Dry purge is the most widely used method for water removal from solid sorbents
Condensation	Water can be condensed in a cold water trap (condenser) held at −10 to 15 °C and located between the sparging vessel and the trap. This technique can be applied to solid and cold trap systems
Hygroscopic trap and drying of the sample	A cartridge packed with hygroscopic salts can be placed in front of the trap to absorb water. If the sample is not an aqueous solution, it is possible to mix it directly with some hygroscopic salt
Permeation	Water from the sample can diffuse through the wall of a drying tube while the analytes stay in the carrier stream. Nafion is the most widely used tubing for the purge and trap technique and for air samples. This method is less attractive due to some selectivity of the Nafion membrane. It has been found that light, polar and oxygenated compounds are partially or completely removed from the stream

During HS extraction there are three phases involved: the condensed phase, its headspace and the SPME polymer. The last phase (SPME fibre) forces compounds out of the matrix (liquid or solid) into the headspace and then into the fibre. The vapour phase should be in equilibrium with the matrix sample to effect headspace sampling of volatiles. The equilibrium of the extraction is reached when the concentration of the analyte is homogenous within each of the three phases [113]. In HS-SPME, a higher temperature may result in less deposition onto the fibre as volatile compounds again favour the vapour phase. This can be a useful tool for selective analysis, as the fibre will favour lower volatility analytes than direct headspace [114].

Headspace solid-phase microextraction has the potential to extract a wide range of organic compounds, volatile or semivolatile, from various matrices, both in their liquid and solid phase. In terms of precision, linearity and sensitivity, HS-SPME equals the HS method.

A new automated HS-SPME sampling device was developed, with the capability of heating the sample matrix and simultaneously cooling the fibre coating. The device was evaluated for the quantitative extraction of polycyclic aromatic hydrocarbons (PAHs) from solid matrices [115]. A simple device consisting of a closed headspace vial equipped with an integral cutting was used for the collection, homogenisation, and HS-SPME sampling. It has been applied for the microscale sampling of volatile monoterpene hydrocarbons from conifer needles [116].

Headspace sorptive extraction (HHSE)

Headspace sorptive extraction (HHSE) was introduced in 2000 by Bicchi et al. [117] and Tienpont et al. [118] as a variant of static headspace analysis with the use of stir bar sorptive extraction (SBSE) to sample the headspace of a sample. This is very similar to HS-SPME, but a coated stir bar is held in the headspace in equilibrium or not with the matrix, for a fixed time, in place of the fibre [119]. After sampling, the stir bar is placed in a glass tube and transferred to a thermo-desorption system where the analytes are thermally recovered and analysed by GC or GC-MS.

The HSSE, compared to other techniques, has high concentration capability, mainly due to the high volume of PDMS. Additionally, PDMS twisters can be applied in both S-HS and D-HS modes for trace analysis and passive sampling.

On the other hand, the main drawbacks of HSSE are the need for dedicated and expensive instrumentations and the lack of “polar” polymer coating for stir bars, to improve HSSE’s effectiveness with medium to high polarity compounds [97].

The combination of HS-SBSE and TD-GC-MS was used for accurate and precise simultaneous determination of mercury and tin organometallic species at the low concentration levels found in many environmental samples. Additionally, the applicability of this method has been proven with a wide range of different samples [120]. Bicchi et al. evaluated the performance of dual-phase twisters for HSSE sampling by analysing the headspace composition of two matrices, i.e. coffee and dried sage leaves [121].

Solid-phase aroma concentrate extraction (SPACE)

Solid-phase aroma concentrate extraction (SPACE) is a modified version of the SPME technique for headspace analysis, with an increased area of the adsorbent to allow more sensitive analysis of volatiles analytes. This new method was introduced by Ishikawa et al. [122]. The SPACE rod used in the technique is fabricated from stainless steel coated with an adsorbent mixture (mainly of graphite carbon). The SPACE rod is fixed on the head of

a closed flask, where it adsorbs the aroma for a given time. Next, the rod is thermally desorbed on-line to the GC or GC-MS system [97]. The SPACE rod collects the analytes with good reproducibility, with the exception of highly polar compounds. The SPACE method proved to have superior capabilities with high concentrations, and it produced a well-balanced chromatogram. This technique has been shown to be successful with roasted coffee beans and other plant matrices [123].

Headspace solid-phase dynamic extraction (HS-SPDE)

The headspace solid-phase dynamic extraction (HS-SPDE) technique was developed by the use of polypyrrole (PPy) sorbent, electropolymerized inside the surface of a needle, as a possible alternative to SPME. In HS-SPDE, analytes are accumulated in the polymer coating of the inner needle wall by pulling in and pushing out a fixed volume of HS to be sampled, through the gas-tight syringe for an appropriate number of times within a fixed time. Because the vapour phase flowing over the accumulating phase layer is continuously renewed, HS-SPDE is a D-HS approach [124]. The trapped analytes are recovered by thermal desorption, employed to transfer the extracted analytes into the GS injection port, and analysed by GC or GC-MS.

A few HS-SPDE applications have been reported in the literature [125]. They are fully automated systems for the analysis of headspace samples (HS-SPDE) [126, 127].

More recently, other approaches based on the same principles known as inside needle dynamic extraction (INDEX) [128] and in-tube extraction (ITEX) [129] have been introduced.

Multiple headspace extraction (MHE)

In 1977, Kolb and Pospisil presented a technique called discontinuous gas extraction [130]. This method was later renamed as multiple headspace extraction (MHE) [131]. This technique involves performing several extractions from a single sample. In this way, the concentration of the analyte decays exponentially and the total peak area corresponding to an exhaustive extraction of the analyte can be calculated as the sum of the areas of each individual extraction. Therefore, the matrix effect is completely removed. Because the MHE procedure follows a logarithmic function, it is not required that the extractions are carried out until all of the analyte is removed from the sample matrix. Instead, the logarithms of the various area values from the consecutive analyses are plotted versus the number of analyses in a linear scale and the total area value is obtained by regression calculation from the areas obtained in only a few extraction steps [132].

Multi HS-SPME has the same aim as MHE. The amount of analyte extracted by the fibre is proportional to the initial amount, and it can be proven that the peak area decays exponentially with the number of extractions. The total peak area can be estimated by performing a few (three or four) successive extractions by HS-SPME [133]. In multi HS-SPME, the relationship between the peak area and the amount of analyte in the fibre coating must be linear over the whole range being studied. Additionally, the distribution constants of the analyte between the fibre and the sample and the volume of the three phases must be constant during all of the extraction steps. The next condition which must be fulfilled to carry out a proper multiple HS-SPME is that equilibrium of the analyte in the three-phase system must be established [134, 135].

Thermal desorption (TD)/thermal extraction (TE)

For environmental reasons and cost, there is great interest in reducing the impact of wet chemical handling in laboratories. This favours heat extraction techniques [91]. Thermal desorption (extraction) is a widely used technique for extracting and isolating semivolatile compounds from various matrices. Almost any sample containing volatile organic compounds can be analysed by using some variation of this technique. This method is well established in environmental analysis, food analysis and forensic science. Thermal extraction provides an attractive alternative to solvent extraction (SE). In the process of TD, heat and inert gas flow (usually helium) are used to extract analytes retained in a sample matrix or on a sorbent bed. A temperature is needed that is high enough to allow desorption of the analytes from the matrix but also low enough to avoid degradation of the sample matrix itself. The analytes are desorbed into the gas stream and are ultimately transferred to the analyzer. Although compounds can be transferred directly from the original sample (sorbent bed) to the analyzer in one thermal desorption step, this simple, single-stage approach has limited practical application [136, 137]. The elution volume required for complete extraction of a typical 100-mg to 1-g sample is too large, giving poor analytical resolution and relatively low sensitivity. TD in its most simple single-stage form is of limited application for packed column chromatography and cannot be used at all for capillary column GC [138]. For this reason, most thermal desorbers are two-stage, i.e. they contain a focusing mechanism (capillary cryofocusing or cold adsorbent trapping) for concentrating analytes desorbed from the matrix (sorbent bed) before releasing them into the analytical system in as small a volume of vapour as possible. Both procedures do produce excellent, capillary-compatible chromatography, but capillary cryofocusing is quite costly in terms of liquid cryogen consumption. Moreover, the volatility range of capillary cryofocusing devices is limited. More

importantly, such systems are prone to blocking with ice during the desorption of humid samples. This procedure is also prone to sample degradation from condensed oxygen. Any blockage or restriction of the desorption gas flow has a significant impact on the efficiency of the process. Thermal desorption as a method of releasing organic compounds from the sorbent bed, or fixed directly from the solid sample matrix, offers the following advantages, in comparison with conventional solvent extraction [139, 140]:

- Typically 1,000 times more sensitivity
- Minimal sample preparation (eliminates the problem of contamination)
- A smaller sample amount is required for the analysis
- No analytical interference from solvent artefacts
- Time efficiency
- Greater than 90% desorption efficiency
- Selective focusing/extraction
- Environmentally friendly (no solvent disposal)
- Cost effectiveness
- Eliminates problem associated with accurate dosing and repetition of the injection of liquid extracts
- Eliminates the appearance of the solvent peak in the chromatogram, the components of which may mask the analytes
- Eliminates difficulties associated with the choice of suitable solvents for the extraction of analytes especially when analytes differ significantly in polarity
- The method is fully automated.

Thermal extraction is not without its limitations, however. Not all types of substrates are suitable for high temperature desorption. The use of TE is therefore complicated by the potential for carry-over, transfer loss, molecular rearrangement, fragmentation or breakdown of more thermally labile analytes at higher extraction temperatures and matrix effects, leading to quantification inaccuracies [141]. Another drawback is sample consumption in a single analysis, although modern TD equipment incorporates design modifications to allow re-collection of split samples in a fresh tube [142].

TD was originally developed as an off-line sampling method with preconcentration of workplace atmosphere by pumping air through a solid adsorbent material [143].

Direct thermal desorption (DTD)

Volatile or semivolatile analytes from liquid or solid samples can also be released by direct thermal desorption (DTD). In the direct thermal desorption technique, a small amount of homogeneous sample is placed directly in a thermal desorption unit. DTD permits the analysis of samples without any prior solvent extraction or other time-consuming sample preparation. Depending on the nature of the materials being tested, samples may be either weighed into empty TD tubes or tube liners for direct desorption.

Direct desorption of analytes from a sample weighed straight into empty desorption tubes or appropriate tube liners is a cost-effective sampling procedure. Sample clean-up, analyte extraction and sample introduction are combined into one automated operation. In addition, since the instrument does not contain a heated transfer line or switching valves it is possible to transfer compounds with a high molecular weight.

Conditions for DTD are [144]:

- High surface area solid materials
- Unrestricted flow of gas through the sample tube
- Sample should be placed well within the heated zone of the thermal desorber
- Molecules should be desorbed intact from the matrix.

DTD is appropriate only if the desired extraction takes place at a temperature below the decomposition point of other materials in the sample matrix and the relatively small sample size that can be measured in a TD tube is representative of the sample as a whole [144].

In 1987, Chen et al. developed a direct sample introduction and thermal desorption GC-MS technique for the analysis of volatile constituents in Chinese medicinal herbs [145]. It offered several distinct advantages: minimal sample preparation, small sample size and short analysis time. Meanwhile, commercial direct sample introduction and thermal desorption devices have become available. This technique is widely applied for the analysis of volatile compounds in plant materials [146–148].

Short-path thermal desorption (SPTD)

Short-path TD, patented by Scientific Instrument Services, Inc. (Ringoes, NJ, USA), is a TD system that sits directly on top of the GC injection port. As a result of the short path of sample flow, these systems eliminate transfer lines, which are contaminated by samples, and optimize the delivery of samples to the GC injector via the shortest path possible [149]. SPTD provides maximum sensitivity by minimizing artefacts, losses and carry-over effects [150].

Temperature-programmed desorption (TPD)

A commercial direct thermodesorption system with a programmable temperature cooled injection system (CIS) and GC-MS for identification has been introduced, which is suitable for the analysis of packed adsorbent tubes and direct analysis of solids and liquids. Gas samples are prepared for analysis by being passed through a desorption tube containing an appropriate adsorbent. All other sample types, placed directly in an empty tube without further preparation, are inserted directly into the desorption

Table 3 Application of solventless sample preparation techniques coupled with TD followed by GC

Target compounds	Medium analysed	Sample preparation		Monitoring objective/key application	Ref.
tert-Butyl alcohol, butyl acetate, toluene, *p*-xylene, *o*-xylene	Workplace atmosphere	OTT – chromatographic column coated with PDMS		Possibility of using a piece of an open-tubular GC column as a trap for isolation and enrichment of organic pollutants in air matrices	[14]
H_2S, MeSH, EtSH, Me_2S, Me_2S_2	Air	SPME (75 μm CAR/PDMS) for 0.25, 0.5, 1.0, 2.0, 4.0, 8.0 and 14.0 h at room temperature		Potential of SPME for TWA sampling of volatile sulfur compounds was investigated	[152]
MeSA	Tomato plant	DTD	5 min at 220 °C	Development a technique of direct sample introduction and TD followed by GC-MS for rapid determination of analytes	[153]
Semivolatile dioxin surrogate compounds	Fly ash		8–16 min at 300 °C	TD-GC-MS technique was tested, optimized and successfully applied for the determination of analytes	[141]
1,4-Dioxane	Food additives		2 min at 135 °C	Development fast, simple, sensitive TD-GC method for determining traces of analytes	[154]
Benzaldehyde, benzyl alcohol, amphetamine, *cis*- and *trans*-1,2-dimethyl-3-phenylaziridine, dimethylamphetamine (DMA), *N*-acetylephedrine	Methamphetamine (MA)		3 min at 120 °C	Identification and profiling of impurities in MA; LLE and TD were compared for impurity profiling of MA	[155]
Organic explosives (nitroaromatics, nitramines, nitroesters)	Wipe materials		3 min at 280 °C	Desorption of nitramine explosive from a PTFE wipe has been demonstrated for the first time	[156]
	Water	DI-SPME	1 μm PPESK – for 30 min at 40 °C	A novel polar SPME fibre coated with PPESK was prepared by immersion precipitation technique; The method is feasible for analysis of nitroaromatic explosives water samples	[157]
			60 μm PDMS/DVB, 75 μm CAR/PDMS, 100 μm PDMS, 85 μm PA – for 30 min at room temperature	Four different SPME fibres were tested to analyse commonly encountered organic explosives	[158]
Hydrocarbons, fatty acids, esters, sulphur compounds, carbonyl compounds	Cheese	PT – p.t.[a] 20 min, p.f.r.[b] 40 ml/min, s.t.[c] 40 °C		Identification of volatile compounds characteristic of Roncal cheese throughout the entire preparation period	[159]
Haloanisoles, volatile phenols	Wine	MHS-SPME (75 μm DVB/CAR/PDMS) for 50 min at 70 °C in 5 consecutive extractions		First application of MHS-SPME procedure to determine the analytes simultaneously in wines	[160]
2,4,6-Trichloroanisole (TCA)	Water	PT – p.t. 30 min, p.f.r. 0.3 l/min		Application of a portable Curie point thermal desorption unit for fast sample heating and injection into the GC	[161]

Chloroanisoles, chlorophenols	Cork	SBSE (0.5 mm PDMS layer; stirring at 700 rpm) for 60 min at room temperature		Method accomplishes the joint determination of an array of compounds and the release of these compounds from the cork [162]
Earthy-musty odorous compounds (2-isopropyl-3-methoxypyrazine, geosmin, 2-isobutyl-3-methoxypyrazine, 2-methylisoborneol, 2,4,6-trichloroanisole)	Water	PT – p.t. 20 min, p.f.r. 35 ml/min		Investigation of the performance of an on-line fully automated PT extraction technique coupled to GC-MS in terms of sensitivity, selectivity, linearity and precision [163]
Monomers, volatile additives	Thermoplastic polymers	PT – p.t. 2, 4, 6, 8, 10 and 12 min; p.f.r. 0.2 l/min; s.t. 20, 40, 60, 80 and 100 °C		PT screening test was developed for the fast localization of the source of emission [164]
1,2-Dibromoethane (EDB), 1,4-dichlorobenzene (PDCB), naphthalene	Honey	PT – p.t. 40 min, p.f.r. 40 ml/min, s.t. 40 °C		First application simultaneous determination of PDCB, EDB and naphthalene residues in honey [165]
Benzene, carbon tetrachloride, 1,2-dichloroethane, 1,1-dichloroethene	Active pharmaceutical ingredient (API)	PT – p.t. variable, p.f.r. 40 ml/min, s.t. 0 °C		PT sample preparation was examined in residual solvents analysis of an API [166]
MeHg, Hg(II)	Water	SBSE (24 µl PDMS layer; stirring at 1,000 rpm)	15 min at 24 °C	Determination of trace amounts of analytes in water by SBSE with in situ alkylation with sodium tetraethylborate [167]
EtHg,MeHg, Hg(II), DiEtHg			60 min at room temperature	Speciation analyses of mercury in drinking water by SBSE with in situ propyl derivatization [168]
5-Chloro-2-(2,4-dichlorophenoxy)phenol	Urine	SBSE (24 µl PDMS layer; stirring at 500 rpm)	60 min at 25 °C	Determination of trace amounts of triclosan in human urine samples by SBSE [169]
	River water		120 min at room temperature	Determination of trace amounts of triclosan in water samples by SBSE without derivatization step [170]
Benzophenone (BP) sunscreen compounds	Water	SBSE (24 µl PDMS layer; stirring at 1,000 rpm) for 120 min at room temperature		Determination of trace amounts of BPs in water samples by SBSE with in situ derivatization [171]
Terpenes, C_{13}-norisoprenoids, C_6 compounds	Wine	SBSE (0.5 mm µl PDMS layer; stirring at 700 rpm) for 90 min at 60 °C		First optimization of wine primary aroma compounds analysis by SBSE in terms of ionic strength, temperature and extraction time [172]
Monoterpenes	Indoor air	Multi-sorbent tubes packed with Tenax TA, Tenax GR, Carbosieve SIII, Chromosorb 106 – active sampling		Comparison of different adsorbents which are often used for VOC monitoring for active air sampling of monoterpenes in indoor air [140]
8 compounds responsible for off-flavours in wine	Wine	SBSE (63 µl PDMS layer; stirring at 900 rpm) for 60 min at room temperature		Optimization of SBSE for the simultaneous quantification of analytes responsible for the most important off-flavours in wine [173]
Organochlorine pesticides, carbamates, organophosphorus pesticides, pyrethroids,	Vegetables, fruit, green tea	SBSE (24 µl PDMS layer; stirring at 1,000 rpm) for 60 min at 24 °C		Optimization and validation of the SBSE-TD-RTL-GC-MS method for the determination of 85 pesticides in vegetables [174]

Table 3 (continued)

Target compounds	Medium analysed	Sample preparation	Monitoring objective/key application	Ref.
4-Hydroxybutyric acid lactone (GBL)	Liquid-phase filling of chocolate containing an aqueous alcoholic cherry-flavoured sugary syrup	SBSE (0.5 mm PDMS layer) for 120 min at room temperature	Confirmation of the possibility of using the SBSE-TD system to evidence small amounts of GBL (natural or added) with high sensitivity and without the use of extraction procedures which can induce loss of extraction yields	[175]
Tetramethylene disulfotetramine (TETS)	Food matrices	SBSE (0.5 mm PDMS layer) for 60 min at room temperature	Description of a method for the determination of tetramine in foods using SBSE-GC-MS	[176]
Ibuprofen	Water	HS – oven temperature 90 °C, equilibration time 60 min	Method for the determination of ibuprofen, as a representative of pharmaceutical compounds, in aqueous samples	[177]
N-(1-Phenethyl-4-piperidyl)propionanilide	Human exhaled air	DI-SPME (PDMS/DVB) for 60 min at 85 °C	Method for detection and quantification of fentanyl from breath samples was developed	[178]
Tetramethylenedisulfotetramine	Urine	DI-SPME (7 and 100 μm PDMS, 80 μm PA) – for 12 min at 50 °C	Application of method to detection of tetramine toxicosis in criminal cases and clinical therapy of poisoned sufferer	[179]
2,6-Diisopropylphenol (propofol)	Human exhaled air, blood	HS-SPME (CAR/PDMS/DVB) for 50 min at 40 °C	Evaluation of a method in terms of reliability, precision and reproducibility for simultaneous propofol determination in patients' blood and exhaled air	[180]
2,3-Dimethyl-2,3-dinitrobutane (DMNB)	Ammonium nitrate matrix	HS-SPME (amide bridged-C[4]/OH-TSO fibre) for 30 s at room temperature (23–27 °C)	First report of an SPME-GC system to extract marking agent in explosives for subsequent detection in a simple, rapid, sensitive manner	[181]
Fungal volatile metabolites	Surface culture fungal	HS-SPME (100 μm PDMS) for 30 min at 25 °C HS-SBSE for 60 min at 25 °C	Analytical method to detect mycotoxin-producing fungi based on the HS analysis of sporulated surface cultures	[182]
Atrazine, ametryn	Water, soil	HS-SPME (PPy-DS) for 45 min at 65 and 70 °C respectively for water and soil	Simple and rapid method for the simultaneous determination of analytes in soil and water samples by ion mobility spectrometry (IMS)	[183]
3-Methylbutanal, pentanal, toluene, 2,4-pentanedione, 3-heptanone, cyclohexanone, 2-ethylhexanal, C_6–C_{11} alcohols	Multilayer flexible packaging	MHS-SPME (75 μm CAR/PDMS) for 60 min at 100 °C in 4 consecutive extractions	VOCs formed in the extrusion–coating process of multilayer packaging materials were quantified	[133]
Amphetamine and amphetamine-like drugs (MA, MDA, MDEA, DMA)	Urine	HS-SPME (100 μm PDMS; stirring at 600 rpm) for 30 min at 95 °C	Sensitive procedure for the determination of amphetamine-like drugs in urine samples was developed by using SPME with an on-fibre derivatization device	[184]

	Hair samples	HS-SPDE (50 μm PDMS/AC; stirring at 650 rpm) for 5 min at 50 °C in 50 consecutive extractions	Automated HS-SPDE coupled with GC-MS was evaluated for the determination of amphetamines and synthetic designer drugs in hair samples	[185]
		HS-SPME (100 μm PDMS) for 5 min at 90 °C	Simple and rapid procedure that can be used for screening purposes	[186]
Cannabinoids (Δ^9-tetrahydrocannabinol, cannabidiol, cannabinol)	Hair samples	HS-SPDE (65 μm PDMS/AC; stirring at 200 rpm) for 25 min at 90 °C in 30 consecutive extractions	Procedure used alkaline hydrolysis and HS-SPDE, followed by on-coating derivatization and GC-MS was evaluated	[187]
	Indoor air	Tenax TA adsorbent tube – active sampling	Development of a simple method based on adsorbent air-sampling system and GC-MS for identification of Δ^9-THC in air, serving as an indicator of marijuana smoking	[188]
δ^{13}C of low molecular VOCs	Air	Tenax TA adsorbent tube – active sampling	Investigation of the usage of a TD-GC-IR-MS method to determine δ^{13}C of VOCs in airborne sample as a means of differentiating their sources in the environment	[189]
Volatile fraction	Fruits, rosemary leaves (*Rosmarinus officinalis* L.), coffee, wines, banana	HS-SPDE (50 μm PDMS) at 35 and 50 °C in 50 consecutive extractions	Preliminary results of a study to optimize HS-SPDE sampling parameters and of HS-SPDE-GC-MS analyses applied to food and aromatic plants	[127]
Volatile fatty acids, phenols, indoles	Cow slurries	PT – (optimized condition) p.t. 20 min, s.t. 80 °C	Optimization of the simultaneous PT concentration of analytes from cow slurries	[190]
Volatile esters	Cider	PT – p.t. 30 min, p.f.r. 50 ml/min, s.t. 20 °C	Development of a PT method to quantify volatile esters in ciders	[191]
26 aromatic volatiles	Wine	PT – p.t. 20 min, p.f.r. 40 ml/min, s.t. ambient temperature	Design of a fast and simple method of analysis by PT coupled to GC-MS for quantification of volatiles in the "basic aroma" and "delicate aromas" of wine	[192]
2-Cyclopentyl-cyclopentanone	Polyamide 6.6	MHS-SPME (65 μm PDMS/DVB) for 45 min at 50, 80 and 120 °C in 2, 5 and 6 consecutive extractions	Investigation of interactions between polar analytes and solid polar matrices and the effect of these interactions on the MHS-SPME analysis	[193]
4-Ethylphenol, 4-ethylguaiacol, 4-vinylphenol, 4-vinylguaiacol	Wine	MHS-SPME (75 μm CW/DVB) for 40 min at 60 °C in 3 consecutive extractions	First application of the MHS-SPME procedure to simultaneous determination of analytes, and the detection and quantification limits	[194]
Methyl ethyl ketone (MEK), isopropyl alcohol (IPA), *N*,*N*-dimethyl formamide (DMF), acetone (ACE), *N*-methyl formamide (NMF)	Saliva	HS-SPME (75 μm CAR/PDMS, stirring at 1,000 rpm) for 5 min at 80 °C	An alternative exposure monitoring method and measurement of multi-component mixtures with different polarities in the saliva sample matrix	[195]
Capsaicin, dihydrocapsaicin	Fabrics	HS-SPME (100 μm PDMS, 65 μm PDMS/DVB, 85 μm CAR/PDMS, 70 μm CW/DVB, and 50/30 μm (DVB/CAR/PDMS) for 20 min	Comparison of SPME method with solvent extraction technique	[196]

Table 3 (continued)

Target compounds	Medium analysed	Sample preparation		Monitoring objective/key application	Ref.
THMs	Ambient air from swimming pool,	Multi-sorbent tubes packed with Tenax TA, Chromosorb 102 or Carbopack B – active sampling		Development and evaluation of a TD-GC-MS method for determination of THMs in the ambient air at a swimming pool	[197]
	Water	PT	p.t. 11 min, p.f.r. 40 ml/min, s.t. room temperature	Comparison of analytical performance of SPME and PT coupled to GC-MS for simultaneous determination of 8 VOCs	[198]
			p.t. 11 min (4–19 cycles); p.f.r. 40 ml/min; s.t. 25, 35 and 50 °C	Study of purge system's efficiency by means of several consecutive purge cycles lasting 11 min, each of the same liquid sample	[199]
VOCs	Ambient air	Multi-sorbent tubes – active sampling	Carbotrap, Carbopack X, Carboxen 569	Development and evaluation of a TD-GC-MS method for determination of a range of VOCs in air for monitoring of air-quality and malodorous episodes	[200]
	Indoor air, ambient air		Carbopack B and Carboxen 1000	This study has yielded up-to-date information on levels of a variety of priority airborne chemicals in residential air, which is being used to estimate current exposure to these substances	[201]
			Tenax TA and Carbopack B	Development of a multiphase assurance approach for the accurate and precise determination of VOCs in different microenvironments	[149]
	Workplace air		Carbopack B, Carbopack Y and Carboxen 1000	Development of a new method for quantification of specific compounds	[202]
	Human exhaled air		Carbograph 1TD/ Carbopack X	More accurate approach of investigating the full range of VOCs in exhaled air and proof of principle by correctly classifying human breath of smokers and non-smokers	[203]
	Indoor air	Adsorbent tube – active sampling	Chromosorb 106	Attempt to identify VOC levels in indoor air of public places when ozonisation units were in use and not in use	[204]
			Carbotrap	Direct toxicity, toxicity after metabolic activation, and effects on the immune system of extracts of motor vehicle indoor air were assayed	[205]
	Butter	PT	p.t. 60 min, p.f.r. 30 ml/min	Evaluation of the performance of PT for analysis of volatile fraction of butter	[206]

	Plant (*Swertia tetraptera*, *Saussurea involucrate*, *S. lacostei*)		p.t. 10 min, p.f.r. 40 ml/min, s.t. 80 °C	Design of an improved PT method for efficiently extracting weak VOCs from herbal medicines [207]
	Tomato	MHS-SPME (75 μm CAR/PDMS) for 50 min at 70 °C in 5 consecutive extractions		First application of MHS-SPME to quantitative determination of aroma components of tomato samples [208]
	Extra-virgin olive oils	DTD	10 min at 70, 175, 250 °C	Combining multi-step DTD and comprehensive GC enables a rapid study of the characteristic classes of compounds emitted when food is treated at different temperatures during its preparation [209]
			20 min at 40 °C	Instrumental performances of a TD-CIS coupled with GC-MS were improved by a Plackett–Burman experimental design for the direct thermal extraction of volatile compounds from extra-virgin olive oils [210]
	Plant (*Ziziphora taurica* subsp. *taurica*)		10 min at 150 °C	Characterization of composition of volatile fractions and comparative evaluation of its composition with regard to the different isolation techniques [211]
	Şekerpare-type apricots		5 min at 150 °C	Identification of changes in profiles of volatiles desorbed when using other drying techniques (sun, hot air, microwaves) [212]
	Essential oil from the hulls of *Pistacia vera* fruits		5 min at 100, 150, 200 250 °C	Identification of a diverse range of chemical classes extracted from a matrix at different desorption temperatures [213]
	Cheddar cheese			Examination of the effect of maturation on composition of Cheddar cheese volatiles [214]
	Hop (*Humulus lupulus* L.) essential oils		5 min at 150 °C	Test of the DTD methodology for essential oil profiling of hops [215]
	Plant (Spanish *Origanum vulgare*)		15 min at 180 °C	Application of DTD-GC-MS to the study of volatile components present in flowers and leaves [216]
	Plant (*Lavandula luisieri*)			Chromatographic profiles of plant volatile fractions were obtained by DTD [147]
	Plant (*Teucrium chamaedrys*)		5 min at 180 °C	Direct quantification of volatiles obtained from the leaves using DTD-GC×GC-TOF-MS [217]
BTEX	Soils	MHS-SPME (75 μm CAR-PDMS) for 20 min at 30 °C in 3 consecutive extractions		Study of parameters affecting extraction by multiple HS-SPME such as the type of fibre, amount of soil, addition of water, temperature and extraction time [218]

Table 3 (continued)

Target compounds	Medium analysed	Sample preparation	Monitoring objective/key application	Ref.
	Seabed sediment	PT – p.t. 10 min, p.f.r. 40 ml/min, s.t. 80 °C	Valid method for determination of biodegradation process of BTEX in seabed sediment	[219]
BTEX, *n*-aldehydes (C_6–C_{10})	Melted snow water	HS-SPDE (65 μm PDMS/AC; stirring at 500 rpm) for 20.5 min at 50 °C in 60 consecutive extractions	Analysis of analytes in matrix based on HS-SPDE-GC-MS and using a cooling device for the needle during extraction	[45]
PAHs	Air	Multi-sorbent tubes packed with PDMS/ Tenax TA – active sampling	A mixed bed sorption/adsorption sampling tube is used and applied to field sampling of 16 EPA PAHs (+benzo[*e*]pyrene) in air	[220]
	Water	DI-SPME (30 and 100 μm PDMS and 85 μm PA, 20 μm PIL) for 60 min	First application of sorbent coatings based on ILs (ionic liquids) in DI-SPME for extraction of water pollutants, and coupling with GC-MS	[221]
		HS-SPDE for 20 min at 80 °C in 200 consecutive extractions	HS-SPDE technique was developed by using polypyrrole (PPy) sorbent, electropolymerized inside the surface of a needle, as a possible alternative to SPME	[124]
PCBs	Water	DI and HS SPME (30 μm PDMS, novel PANI); the extraction time and temperature ranged from 20 to 60 min and from 50 to 85 °C respectively	Development of SPME method to use as a simple, rapid and inexpensive solution for determination of PCBs at ultra-trace level in water samples	[222]
	Sediment	HS-SPME (100 μm PDMS) for 10 min at 100 °C min	Development a fast procedure for screening PCBs in sediments combining the advantages of the SPME technique and narrow-bore GC columns	[223]

TWA time-weighted average, *MeSA* methyl salicylate, *LLE* liquid–liquid extraction, *DI* direct immersion, *PPESK* poly(phthalazinone ether sulfoneketone), *MHS* multiple headspace, *RTL* retention time locked, *MDA* 3,4-methylenedioxyamphetamine, *MDEA* 3,4-methylenedioxy-*N*-ethylamphetamine, *THM* trihalomethane, *TOF* time of flight, *PIL* polymeric ionic liquid, *PCB* polychlorinated biphenyls, *PANI* polyaniline

[a] Time of purge and trap

[b] Flow of purging gas

[c] Sample temperature

Table 4 Advantages, disadvantages and conditions used to optimize solventless extraction techniques

Sample preparation technique	Advantages	Disadvantages	Conditions used to optimize sample extraction step
Open-tubular trapping (OTT)	Sample cross-contamination and possible degradation are minimized	Low retention power for the trapping of very polar compounds from aqueous samples	Type of capillary coatings
	Complete removal of water from the trap	Complex instrumental set-up and unfavourable sampling conditions	Sampling flow rate
	Very volatile compounds can be enriched at ambient temperatures	Long sampling time for large sample volumes	
	Overcomes mechanical stability problems inherent to conventional SPME fibres		
Solid-phase microextraction (SPME)	Rapidity, simplicity, sensitivity	Limited range of stationary phases	Extraction and desorption parameters (temperature, time)
	Compatibility with analyte separation and detection by different systems	Relatively low operating temperature	Type and thickness of fibre coating
	Provides linear results for a wide concentration of analytes	Breakage of the fibre	Sample properties (pH, ionic strength), sample agitation
	Small in size (convenient for designing portable devices)	Stripping of coatings	Sampling mode
		Bending of the needle (expensive)	Derivatization conditions
		Batch to batch variation of fibre coatings	
		Robustness of fibre coatings	
		Calibration must be made with the same solutions and/or samples	
In-needle solid-phase microextraction	High sorption capacity	Limited range of stationary phases	The ways of immobilizing a sorbent in the needle
	No bleeding from thick-film coatings		
Inside needle capillary adsorption trap (INCAT)	Simple methodology and easiness; rapidity of the analyses	Competitive effects and variation in sampling efficiencies for the analytes	Packing single and multiple-layer sorbent beds
		Low capacity of the sorbent	Applying different desorption strategies to the GC injector
		Elution zones of analytes are slightly dispersed	
Needle trap devices (NTD)	Needle-like devices are particularly convenient for automation and development of on-line procedures	Limited range of stationary phases	Desorption time and temperature
			Sampling flow rate and breakthrough volumes
	Inexpensive, robust and reusable		
Solid-phase dynamic extraction (SPDE)	Sensitivity is better and competition effects are largely eliminated compared to SPME	Limited range of stationary phases	Extraction phase
		Desorption temperature is limited by GC injection port	Parameters of extraction and desorption
	High concentration factors		
	Easy to apply and automate		
Stir bar sorptive extraction (SBSE)	High enrichment factor compared to SPME	Limited range of stationary phases	Type and thickness of the coating
		Specially designed thermal desorption units involve use of relatively sophisticated instrumentation	Extraction time
			Sample properties
			Agitation
		Manual transfer of stir bar to the desorption unit may cause partial loss of the sensitivity gained	Temperature and analyte desorption
Gum-phase extraction (GPE)	Straightforward, simple and matrix-independent calibration	Often fails for weakly retained solutes	Extraction phase
	Increase in sensitivity can occur, compared with the OTT trap and an SPME fibre		Parameters of extraction and desorption
Equilibrium gum-phase extraction (EGPE)	Achieved a higher sensitivity for all compounds than GPE	Expense of the more complicated calibration	
Closed-loop stripping analysis (CLSA)	Rapid and simple method for VOCs determination	Reproducibility problems	Operational parameters: time, temperature, stream of inert gas
		CLSA is also not able to avoid foaming problems during analysis of waters with higher surfactant concentrations	
Sorption tubes	High sampling versatility	Sorption and desorption efficiencies may not be 100%	Type of sorbent
	High VOC concentration power		Sampling volume, rates, time
	Easy portability	Background impurities in sorbent tubes may interfere with analytes	

Table 4 (continued)

Sample preparation technique	Advantages	Disadvantages	Conditions used to optimize sample extraction step
	Low cost and easy storage	Limitations of sampling volume, rate, time	
		Influence of sampling conditions on efficiency of sorption of analytes	
Static headspace (S-HS)	Easy to use	Lack of sensitivity	Oven temperature
	Volatile compounds in almost any sample matrix can be extracted	Determination of trace compounds of relatively large molecular weight is very limited	Equilibration time
	Sample extraction, clean-up and preconcentration steps are not necessary		Vial pressurization
			Speed and time agitation
Dynamic headspace (D-HS)	Highly reproducible and automated extraction procedure	Adsorption of water on trap	Sampling temperature
			Desorption temperature and desorption gas flow rate
Headspace solid-phase microextraction (HS-SPME)	Simplicity, portability and low cost	Limited range of stationary phases	Temperature and time of heating
	Shortens the time of extraction		Time of exposure of the fibre in the headspace
	Facilitates analysis of solid samples		Mass of salts added to matrix
Headspace sorptive extraction (HHSE)	Amounts of analyte presented in the headspace sampled by the twister can be easily determined	Need for dedicated and expensive instrumentations	Type of mode
	Can be used to sample headspace with unfavourable β values and/or large headspace volumes	Limited range of stationary phases	Type of trapping phases
	High concentration capability		Volume of PDMS
			Temperature and time of heating
			Speed and time of agitation

chamber. After purging with the carrier gas and heating to the desired temperature, the analytes are transferred into the CIS for cryofocusing. After complete desorption, the CIS liner is then heated to the desired temperature to allow transfer of the trapped analytes to the analytical column [151].

Advantages of direct desorption of volatile trace compounds by TD-CIS-GC-MS are [91]:

- Universal applicability of GC-MS to all sample matrices (gaseous, liquid or solid)
- Solvent-free analysis of complex matrices
- Wide boiling point range of analytes (usually C_2 to C_{40}, but up to C_{100} in a modern multimode injection system)
- Complete transfer of high-boiling analytes
- Lower detection limits through large volume injection
- Allowance for large concentration ranges through the use of split, splitless or solvent venting modes
- Avoidance of cross-contamination
- Preparation of standards and samples by spiking solutions onto the desorption tube
- Autosampler capability
- High desorption flow allowing fast analysis times

Application of solventless sample preparation techniques for the analysis of environmental contaminants in different matrices

It should be noted that there is no universal sample technique suitable for all types of sample. Sample preparation is dependent on the nature of the sample's analytes, matrix, final separation method and the type of information which is sought. For this reason, a number of different sample preparation (extraction) techniques exist, each suited to a different analyte and matrix type. Table 3 lists the application of solventless sample preparation techniques for the analysis of contaminants in the different matrices coupled with TD followed by GC, sorted by analyte.

Concluding remarks and future trends

Research trends in solventless sample preparation techniques based on solid- and vapour-phase extraction for the analysis of environmental contaminants in different matrices are focused on studying new resolutions for higher extraction efficiencies, selectivity and stability. The development of new devices to improve the sampling process and the study

of novel calibration processes are considered. Trends in instrumentation indicate focus on improved automation and ruggedness, field portability and novel selectivity for specific applications. Recent trends focus on the minimization of the use of organic solvents in sample preparation, automation, and speeding up sample preparation procedures. This means that the application of solventless sample preparation for different fields continues to increase.

Table 4 summarizes the main advantages and disadvantages of the techniques discussed, including the conditions used and/or parameters adjusted to optimize the sample extraction step.

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