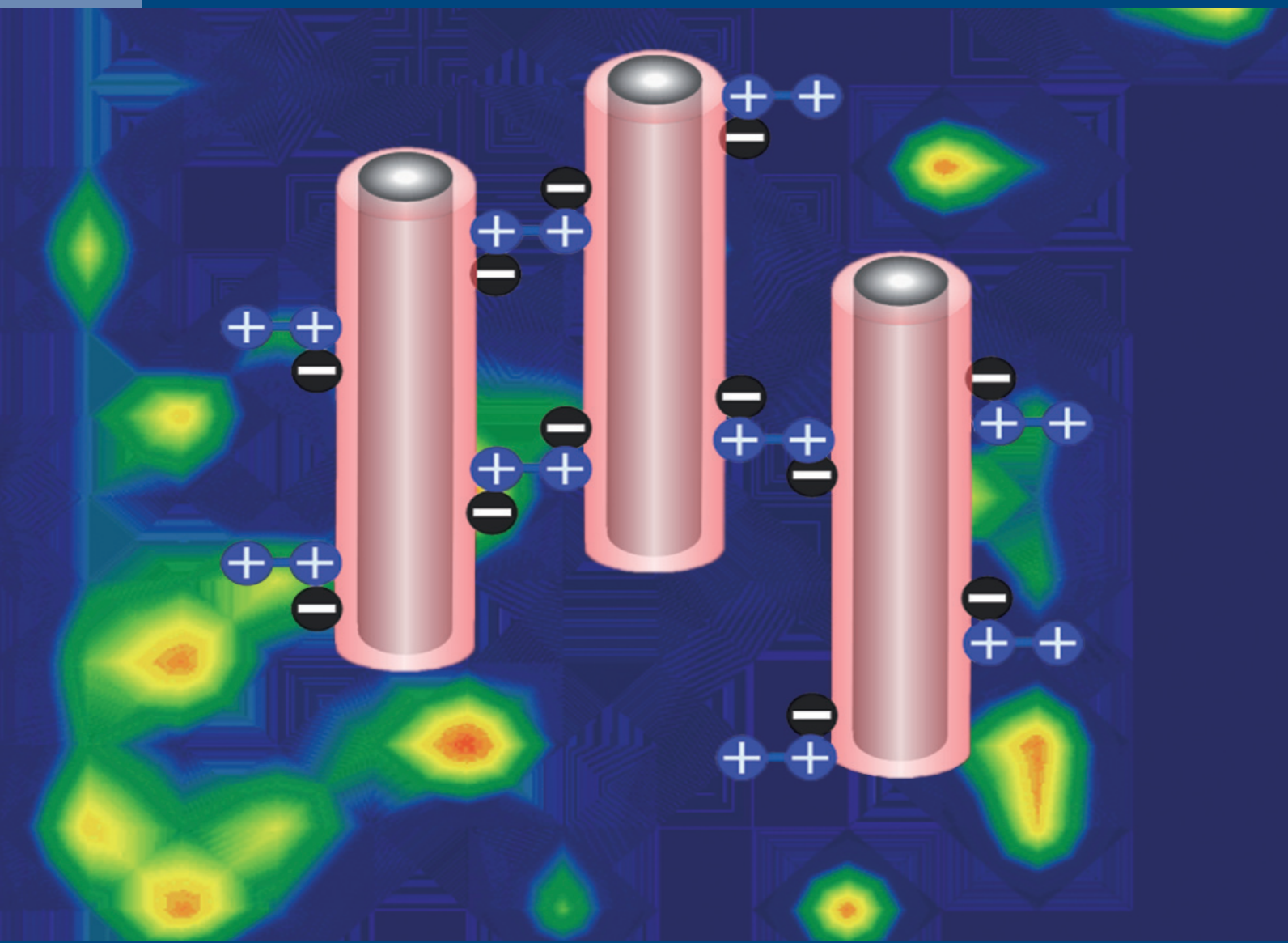
ISSN 1615-9306 · JSSCCJ 42 (1) 1–458 (2019) · Vol. 42 · No. 1 · January 2019 · D 10609

JSS

JOURNAL OF SEPARATION SCIENCE

1|19



Methods
Chromatography · Electroseparation

Applications
Biomedicine · Foods · Environment

www.jss-journal.com

WILEY-VCH

Received: 27 August 2018 | Revised: 2 October 2018 | Accepted: 2 October 2018

DOI: 10.1002/jssc.201800902

REVIEW ARTICLE

JOURNAL OF SEPARATION SCIENCE

Critical evaluation of microextraction pretreatment techniques – Part 1: Single drop and sorbent-based techniques

Martina Havlikova[1] | Radomir Cabala[1,2] | Vera Pacakova[1] | Miroslava Bursova[1,2] | Zuzana Bosakova[1]

[1]Faculty of Science, Department of Analytical Chemistry, Charles University, Prague 2, Czech Republic

[2]Toxicology Department, Institute of Forensic Medicine and Toxicology, General University Hospital in Prague and 1st Faculty of Medicine of Charles University, Prague 2, Czech Republic

Correspondence
Dr. Zuzana Bosakova, Department of Analytical Chemistry, Faculty of Science, Charles University, Hlavova 8, Prague 2, 12843 Czech Republic.
Email: zuzana.bosakova@natur.cuni.cz

Sample pretreatment techniques or preconcentration constitute a very important step before the analysis of environmental, clinical, pharmaceutical, and other complex samples. Thanks to extraction techniques it is possible to achieve higher method sensitivities and selectivities. Miniaturization microextraction methods make them more environmentally friendly and only small amounts of samples are required. In the past 30 years, a number of microextraction methods have been developed and used and are documented in thousands of articles. Many reviews have been written focusing on their use in specified professional fields or on the latest trends. Unfortunately, no uniform nomenclature has been introduced for these methods. Therefore, this review attempts to classify all the essential microextraction techniques and describes their advantages, disadvantages, and the latest innovations. The methods are divided into two main groups: single drop and sorbent-based techniques according to the type of extraction phase.

KEYWORDS
liquid phase microextraction, single drop microextraction, solid phase microextraction

1 | CLASSIFICATION OF MICROEXTRACTION TECHNIQUES

SPME, which was developed by Arthur and co-workers in 1990 [1], was one of the first successful preconcentration methods which could be described as microextraction. At present, SPME is widely accepted as a reference or standard for other microextraction methods. SPME is based on the transport of analytes from the sample to a stationary phase, located on the surface of a fiber (which is mostly made from silica) in the SPME holder [2]. Briefly, the advantages of the SPME method are its simplicity, speed of extraction, and the possibility of automation. Its disadvantages include its cost and the fragility of commercial fibers and relatively narrow selection of stationary phase types. These deficiencies led to the development of other types of preconcentration techniques, commonly called liquid-liquid microextraction (LLME) or LPME [3].

The first LLME method was introduced in 1996 and since then other principles of analyte preconcentration [3,4] have been described in the literature. It is difficult to exactly differentiate and distinguish amongst all the published microextraction techniques, because their principles or practical implementation are similar or differ only in a few details. We decided to classify these methods in main groups according to selected criteria. From practical procedure's point of view, we can distinguish: (1) single drop microextraction (SDME) [3,4], (2) membrane-based microextraction [5], (3) homogenous phase-based microextraction [6], and (4) sorbent-based microextraction [7]. In addition, we can further

Article Related Abbreviations: CFME, continuous flow microextraction; DDSME, drop-to-drop solvent microextraction; DI-SDME, direct immersion single drop microextraction; DSDME, directly suspended droplet microextraction; HS-SDME, headspace single drop microextraction; IL, ionic liquid; LLLME, liquid-liquid-liquid microextraction; LLME, liquid-liquid microextraction; SD-LPME, solid-drop liquid phase microextraction; SDME, single drop microextraction

 © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

classify these methods according to the number of phases employed: two-phase and three-phase microextraction. In the two-phase arrangement, the analytes are extracted from a sample (donor phase) directly into an organic solvent (acceptor phase). In the three-phase mode, the analytes are extracted from a sample into an organic solvent and further re-extracted into another solvent [8]. The LLME method may also be arranged according to the movement of the extraction solvent: static and dynamic. In our classification, the static approach means that the acceptor phase is situated in a fixed place, while in the dynamic configuration it moves with the sample [9]; therefore, the sample movement can be ignored. The majority of microextraction methods are non-exhaustive which means that the goal of the method is not to extract all the analyte mass from the sample but to reach distribution equilibrium. It enables the highest possible analyte concentration in a relatively small amount of acceptor phase [10]. To facilitate the analyte transfer between the phases, various types of sample mixing (stirring by a magnetic stirrer, ultrasound or shakers) and heating (infrared or microwave radiation) are used [11]. Another possibility is derivatization of analytes to increase their volatility or solubility in organic solvents [10].

Of course, other parameters are also applicable for method classification but those mentioned above are the most important for understanding the substantial differences among them.

2 | SDME

SDME is one of the oldest LLME methods introduced in 1996 [3]. SDME is a preconcentration technique utilizing a small volume (typically one drop) of an organic solvent immiscible with water immersed in a liquid sample (two phase system) or positioned in its headspace (three phase system). After extraction, the organic phase is collected using a syringe and used for the analyte determination. The SDME method is non-exhaustive [3,4], i.e., it allows repeated extractions of a single sample. Headspace and direct immersion SDME are applicable for analyses of large number of analytes; they are technically simple, cost- and time-saving, and can easily be fully automated [8]. Another advantage is that there is no sample carryover (new extraction solvent with each sample) and only a common laboratory syringe is required. The original SDME format suffered from partial solubility of the organic solvents in water, limited extraction drop volume and its volatility and dislodgement. [10]

Direct immersion SDME (DI-SDME) [3], continuous flow microextraction (CFME) [12], drop-to-drop solvent microextraction (DDSME) [13], directly suspended droplet microextraction (DSDME) [14], and solid-drop LPME [15] belong to the group of two-phase SDME-based methods (liquid sample/acceptor solvent).

Headspace SDME (HS-SDME) [16], liquid-liquid-liquid microextraction (LLLME) [17], and directly suspended droplet microextraction with LLLME [18] belong to SDME methods using three phases (liquid sample/transitional phase/acceptor phase).

2.1 | DI-SDME

The DI-SDME method (static, two-phase) is based on direct immersion of one drop of organic solvent in a liquid sample with a volume of 0.3–40 mL. The droplet is created at the tip of a syringe needle before the extraction and is carefully immersed in the liquid sample. Gentle sample stirring supports the extraction of analytes into the droplet. After extraction, the drop is easily drawn into a microsyringe and then transferred to the separation system [8]. The selection of an organic solvent which is not miscible with water (sample) is a critical step [4,19]. The main advantage of the method is the extraction speed and negligible amount (0.3–3 μL) of high-purity solvent used, which makes it a low-cost "green" method. The disadvantages of DI-SDME are the droplet instability at high stirring speeds and at elevated temperatures and partial solvent solubility in the liquid sample [8]. The small volume of the acceptor solvent (commonly several microliters) limits the number of analysis repetitions. DI-SDME usually utilizes non-polar or weakly polar extraction solvents (e.g. toluene, hexane, chloroform, and octane) for aqueous samples, allowing preconcentration of non-polar or weakly polar analytes, which are moreover compatible with GC. To overcome problems especially with drop instability etc., ionic liquids (ILs) with partial solubility in water, low or negligible volatility, and high viscosity are used.

ILs belong to a class of non-molecular ionic solvents (salts in a liquid state) with low melting points. Their composition is a combination of organic cations and various anions. ILs exhibit "structural tunability", i.e. their viscosity and surface tension can be easily tuned and manipulated [20] to make them less volatile and to form larger and stable microdrops (greater viscosities), which adhere more strongly to the needle and therefore can be used at elevated extraction temperatures [21]. Their disadvantage is poor compatibility with direct injection into a GC (modification of the injection inlet is needed [22]) and questionable toxicity and biodegradability. To increase the extraction efficiency for analysis of polar heterocyclic substances [23], a small amount of carbon nanotubes was added in the IL to stabilize the drop. However, additional diluting and centrifugation of the extract to remove the nanotubes has to be included.

Because the size of the solvent drop significantly depends on the needle parameters, many syringe needle tip modifications were invented. To obtain a larger surface area of the needle tip, a rolled PTFE (Teflon) tube was added to the needle tip [24] or a bell-shaped device [25] was invented,

which hold the solvent inside the device during the whole procedure and the both modifications allow to create a larger drop without loss of extraction solvent.

Classical DI-SDME can also be easily and completely automated. The commercial instrumentation exists since 2007, is suitable for several modes, and has been used for the analysis of benzene hydrocarbons and polycyclic aromatic hydrocarbons. A dynamic SDME mode proved very useful with the advantage of a periodically renewed drop during extraction. This system allows for better extraction efficiency than the static mode [26].

An automated system can form a perfect drop, always with the same size and without bubbles. However, Williams et al. [27,28] found that the presence of bubbles in the drop can be advantageous and enhance the efficiency of extraction. When they added a constant volume of air to the drop, the drops became more stable (increase in buoyancy) and the surface area of the drop was enlarged. Moreover, this technique can also be fully automated.

2.2 | Dynamic LPME

The inclusion of this method, based on the extraction of analytes from an aqueous phase into a thin film of organic solvent immobilized on the inner surface of a syringe glass body, in SDME is not straightforward. Typically, the organic solvent film is created by drawing in a small volume of solvent (drop with a volume of 1–3 μL) before aspiration of the aqueous sample. Subsequent repetitive loading and unloading of the aqueous sample by the syringe piston, while maintaining the extraction solvent inside the syringe, leads to the extraction of the sample analytes into the solvent film [9]. After the last sample unloading, the remaining solvent drop with the extracted analytes is used for the analysis. Therefore, dynamic LPME is more suitable for organic solvents that do not form stable droplets (e.g. chloroform), because it prevents its loss. This method can be fully automated including online mixing of the sample solution to accelerate establishment of the extraction equilibrium [29]. On the other hand, this technique is not applicable for dirty, complex or biological samples, like blood or wastewater [26].

2.3 | DDSME

DDSME is a modification of DI-SDME which is suitable in situations where only a very small volume or complex sample is available, such as biological samples (blood, urine, saliva). In general, DDSME utilizes a hanging drop of organic solvent immersed in the sample drop (both with volumes of tens of microliters). This arrangement ensures fast equilibration between the two phases and therefore does not need stirring. The volume ratio of organic to aqueous sample droplet is greater than for DI-SDME and therefore the preconcentration factor is lower. This method appears to be closest to the exhaustive extraction methods. The first analysis using this configuration was carried out in 2006 in combination with GC-MS [13,30]. MALDI-MS is another popular analytical technique suitable for this extraction method [31]. If the extraction is moreover dynamic, the movement of the aqueous phase in and out of the micro-syringe increases the transfer and diffusion rates of the analyte from the aqueous phase to the organic phase [32]. There is no need for stirring during the extraction; however Zhang et al. [33] developed ultrasonic-assisted DDSME in a capillary tube using ultrasound to support multiple extractions.

2.4 | CFME

CFME was first described in 2000 and the method improved the mass transfer between the organic and aqueous phases [12]. CFME is a two-phase static extraction method based on the extraction of analytes into a single drop of organic solvent, which is in contact with the flowing sample. Commonly, the solvent drop is placed at the top of vertically positioned PEEK tubing through which the sample flows. The capillary and the droplet are placed in a small flow-

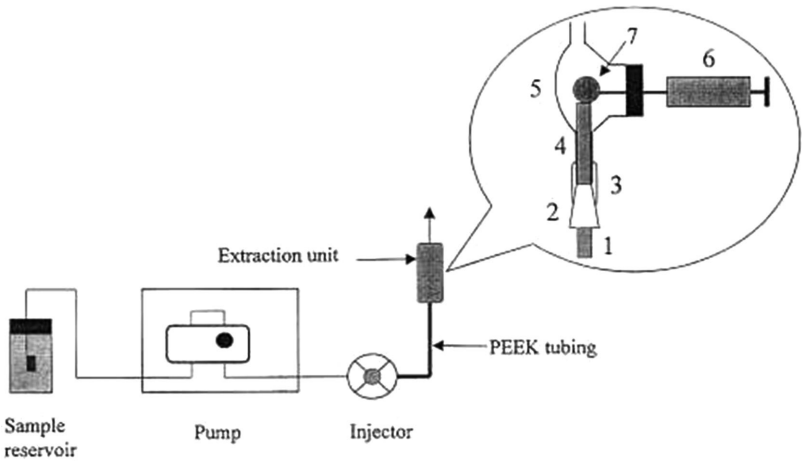


FIGURE 1 Assembly of continuous-flow microextraction system. (1), connecting PEEK tubing, inserted into the extraction chamber; (2), modified pipet tip; (3) "o"-ring; (4) inlet of extraction chamber; (5), extraction chamber; (6) microsyringe; (7) solvent drop. [12]

through extraction chamber (Figure 1). The microextraction procedure can be controlled by the type and volume of extraction solvent, extraction time, flow rate of the sample, its volume, salt concentration, and capillary material. Disadvantages of CFME include the use of non-standard equipment and limitation of the extraction only to a non-polar or slightly polar compounds [12,34], because only non-polar solvents are sufficiently stable in the flowing setup. It is also important to avoid the formation of bubbles in the solution by selection of a suitable pump [35]. Several years ago, systems very similar to CFMEs were developed, but they worked differently and were not termed CFME. In 1995, a method was developed where a steam of gases flowed across a drop of extraction solvent [36]. A year later, a new extraction system was reported, based on an organic microdrop, which was suspended inside a flowing aqueous drop from which the analyte was extracted and the aqueous drop around the organic phase was continuously renewed [4]. At present, efforts are focused on automation and further miniaturization of the CFME method.

2.5 | DSDME

DSDME procedure, classified as two-phase, was developed in 2006. It is based on extraction of the analyte into a suspended solvent droplet (5–100 μL) flowing in the center of stirred sample solution of several milliliters [14]. The stirring and increased contact surface area facilitate the mass transfer of analytes into the solvent. A disadvantage of this method is the tricky collection of the organic solvent after the extraction because it forms a thin layer of organic solvent or may be dispersed within the aqueous sample [37,38]. The solvent must be less dense than the sample solution, so that chlorinated solvents and some IL cannot be used; solvents of low solubility in water and with low vapor pressure to prevent loss during extraction should be employed [39]. Typical extraction solvents are iso-octane or toluene [10]. Pytlakowska et al. [40] pointed out that it is better to shake the extracted solvents rather than use a vortex. The DSDME method is faster than classic LPME, cheaper, more sensitive, and without memory effects, compared to SPME.

2.6 | SD-LPME

Another name for SD-LPME is solidification of the floating organic drop microextraction [41]. SD-LPME was developed in 2007 [15] and is based on a small volume drop (5–200 μL) of an organic solvent dispersed on the surface of a stirred aqueous solution [42]. The organic solvent must have a lower density than water, melting point in the range 10–30°C (e.g. 1-undecanol, 1- and 2-dodecanol, *n*-hexadecane) because after the extraction, the extraction vial is cooled in an ice bath where the solvent drop freezes and can easily be removed mechanically from the surface of an aqueous sample. Then the frozen organic phase is rapidly transferred into a clean vial, thawed at room temperature, and analyzed. The advantages of SD-LPME are its simplicity, low cost, high speed and high preconcentration factors (the drop can be smaller), ability to use high stirring speed and no memory effect due to a fresh portion of organic solvent in each analysis. The disadvantages are a limited selection of suitable organic solvents, possible contamination of the organic phase by the aqueous sample, and the limited potential for automating this method [41,43]. Liquids with a higher melting temperature are not entirely suitable for GC analysis, because they cause signal loss (the evaporation temperature is too high). A modification was therefore developed. Lower boiling solvent *p*-xylene was mixed with 1-dodecanol in a ratio such that the drop was still stable but the extract evaporated at lower temperature, which is advantageous for GC. Moreover, Guo et al. [44] used a chelating agent for better extraction of heavy metal ions. It can be seen that there are many ways to influence the extraction, such as varying the type of solvent, its volume, addition of salt, stirring rate, temperature, etc. To improve the efficiency, Pelit et al. [45] performed the extraction with 2-dodecanol at a temperature of 70°C. All the options, advantages and disadvantages are summarized by Ghambarian et al. in a review [42].

2.7 | HS-SDME

HS-SDME method is the simplest form of SDME with all its benefits and disadvantages (see above), which is suitable for preconcentration of volatile compounds into a solvent microdrop hanging on the tip of a syringe in a gas phase over the liquid or solid sample. In this procedure, the volatile analytes are partitioned among three phases (liquid or solid sample/headspace/organic droplet). After the extraction, the droplet is drawn into the syringe barrel and analyzed, usually by GC or HPLC. The HS-SDME method is useful for analyzing complex samples, because the non-volatile and particulate sample components cannot contaminate the analytical system because the drop is not in direct contact with the sample solvent. Another advantage compared to DI-SDME is based on the possibility of using higher stirring rates of the sample. Organic solvents, such as *n*-octanol, hexadecane, dodecane, and decane, are most often used for HS-SDME [8,10,16]. The static method was first employed by Tankeviciute et al. [46] in 2001 for analysis of alcohols in stirred liquid samples by GC. Lee et al. [47] introduced a very innovative and simple connection by directly coupling HS-SDME with CE. They placed a fused silica capillary filled with a basic running buffer (without the formation of a drop) in the headspace above an acidic donor solution and volatile acidic analytes were extracted into the acceptor phase in the capillary. After extraction, electrophoresis was carried out on the extracts in the capillary.

Dynamic HS-LPME could be performed in two modes – exposed or unexposed. When the drop of solvent is cre-

ated as in static HS-SDME but the drop is repeatedly moved back into the syringe and re-exposed to the sample solution, this is called exposed dynamic HS-LPME. During unexposed dynamic HS-LPME, the extraction solvent is inside the syringe during whole extraction and the gaseous sample is drawn into the barrel and ejected repeatedly [26,38]. The main advantages are the possibility to use solvents which form less stable drops and more exhaustive extraction because the surface of the drop is repeatedly renewed, increasing the transfer of the analyte [10]. These methods were fully automated in commercial autosamplers in combination with GC-MS more than ten years ago and a comparison of the individual techniques was published [26,48].

This technique leads to predominance of the most volatile components, which will be extracted. Therefore, it is sometimes necessary to increase the volatility of the analytes by derivatization [49]. The types of derivatization procedures which are compatible with headspace sampling were summarized by Farajzadeh et al. [50].

2.8 | LLLME

LLLME is a three-phase modification/combination of DSDME and DI-SDME that is often called solvent microextraction with simultaneous back-extraction, carried out by two consecutive extractions. In addition to DSDME, in this method a second drop of aqueous solvent hanging on a syringe needle tip is immersed in a larger organic solvent drop (drop in drop), which floats at the vortex center of a stirred sample [51,52]. The requirements for the extraction are: (a) the organic solvent and water are not miscible; (b) the organic liquid is of lower density than water. The most frequently used solvents are toluene, *n*-octane, 1-octanol, *n*-hexane. The advantages of this setup are a higher level of sample cleanup and higher preconcentration factors, both resulting in lower detection limits [8]. Ma and Cantwell [53] developed simultaneous forward- and back-extraction from a water sample into an aqueous phase across a microliter-sized organic liquid membrane in 1998 and a year later they carried this out with smaller volumes of extraction solvents [54]. For successful extraction, it is necessary to change the analyte affinity for the organic phase by, e.g., protonation, complexation, etc., so it can be easily back-extracted into the aqueous phase [55]. Typically, acidic or polar analytes are extracted from water over an organic phase into a final acceptor solution that is acidic (for basic analytes) or basic (for acidic analytes). In the first step, the uncharged analyte is extracted from the aqueous sample at a properly adjusted pH into a small volume of organic phase (several hundred microliters) floating on the stirred sample. Then the analyte is extracted into an aqueous droplet whose pH is adjusted to a value at which the analyte is ionized and cannot move back into the organic phase [17]. There is also an option where one of the phases contains some derivation agent [51]. The final extract can then be easily analyzed by HPLC or CE without matrix interferences due to its aqueous character. In general, this mode is best suited for extraction of phenols, fatty acids or amines and the analysis of alkaloids in urine by CE [52] can be an example. This method is also known under other names, such as "single drop liquid-liquid-liquid microextraction" [56] or "three-phase liquid-phase microextraction" [57].

2.9 | Directly suspended droplet liquid-liquid-liquid microextraction

This method is related to LLLME and is based on the same principles. In directly suspended droplet LLLME, the droplet of the aqueous phase, used for the back extraction of the analytes from the organic phase, is not hanging on the syringe needle tip but is directly suspended in the organic phase. After back extraction, the major part of the droplet is drawn into the syringe and analyzed [58–60]. This method is also known under another name: "directly suspended droplet three liquid phase microextraction" [18].

2.10 | Solvent supported microextraction

Solution of the difficulties associated with the drop stability, limitation of its volume and drop-solvent surface led to the use of a solid matrix to support the extraction solvent drop [10]. This solvent supported microextraction method is related to SDME techniques because only a few microliter of solvent are used. The method involves the use of various supports for the extraction solvent. The cheapest support used was a short piece of knitting-wool fiber, which was held by hook. An extraction solvent was injected in it and the fiber was placed in the sample. After 30 min, the fiber was removed and extracted by acetonitrile in a HPLC vial [61]. Saraji et al. [62] used a stainless-steel wire coated with silica microstructure for better adhesion of the extraction solvent. The wire was dipped into the extraction solvent, was then exposed to the sample solution and was finally inserted into the GC injection port to desorb the extracted sample. This approach is similar to the SPME methodology (described further) but has some advantages, such as the absence of carry-over problems (the extraction solvent is renewed each time) or the mechanical stability of the wire.

This method can also be used in the headspace mode to overcome problems related to the stability and solubility of the extraction solvent. Ho et al. [63] exploited the advantages of SPME, reused the spent SPME fiber and coated it with an IL solution film. A great advantage of these methods is also that the extraction solvents can be easily and rapidly changed according to the requirements of the analysis.

The detailed theory and some practical information about the briefly described SDME methods are listed in a number

TABLE 1 Summary of possible modifications of single drop microextraction techniques

Modification	Commonly used abbreviation	Review where the methodology is mentioned	First or significant application of the methodology
Direct immersion single drop microextraction	DI-SDME	Jeannot et al. [8]	Jeannot and Cantwell [3]
Dynamic liquid phase microextraction	Dynamic-LPME	Sarafraz-Yazdi and Amiri [67]	He and Lee [9]
Drop-to-drop solvent microextraction	DDSME	Jain and Verma [38]	Wu et al. [13]
Continuous flow microextraction	CFME	Xu et al. [66]	Liu and Dasgupta [4]; Liu and Lee [12]
Directly suspended droplet microextraction	DSDME	Jain and Verma [38]	Lu et al. [14]
Solid-drop liquid phase microextraction/Solidification of organic drop microextraction	SD-LPME/SFODME	Ghambarian et al. [42]; Ganjali et al. [43]	Zanjani et al. [15]
Headspace single drop microextraction	HS-SDME	Xu et al. [66]; Jeannot et al. [8]	Tankeviciute et al. [46]; Theis et al. [16]
(Single drop) Liquid-liquid-liquid microextraction/Solvent microextraction with simultaneous back-extraction	LLLME	Jain and Verma [38]	Ma and Cantwell [53]; Ma and Cantwell [54]
Directly suspended droplet liquid-liquid-liquid microextraction/Directly suspended droplet three liquid phase microextraction	DSD-LLLME	Jain and Verma [38]	Sarafraz-Yazdi et al. [18]
Solvent supported microextraction (without the use of a membrane)	SSME	Kokosa [10]	Zhang and Lee [61]; Saraji and Farajmand [62]

of articles and reviews [8,10,38,51,64–67]. The specific literature on individual methodologies is summarized in Table 1. Other literature sources describe the determination of pollutants [68], pesticides [5,69], drugs [70,71] or inorganic compounds [72]. Another group of reviews summarizes the application of microextraction techniques for analysis of various compounds in foodstuffs [39], in natural products [73] or in water and wine [74]. Ocana-Gonzáles et al. [75] summarized the use of all microextraction techniques in bioanalysis. The newest trend in SDME is utilization of ILs as the extraction phase, which is described in detail in a review article [76].

3 | SORBENT-BASED MICROEXTRACTION

SPME was the first microextraction and preconcentration method and was developed almost 30 years ago [1]. The basic principle is based on the interaction (adsorption or absorption) between the extraction phase and the analyte. According to the shape of the extraction phase and method employed, this technique could be divided into several groups (see Table 2). The oldest and most popular mode is fiber-based SPME [77]. The configuration of the method is quite simple. A small amount/volume of polymeric extraction phase is required, and is mainly immobilized on fused-silica fibers. The fiber is connected to a syringe plunger and can be protected by pulling them inside the syringe [78]. This device is readily available commercially. A small sample amount is required and various samples can be employed – aqueous, gaseous, solid or complex samples. The sample preparation is minimal and the extraction step can be carried out anywhere [7]. According to the arrangement of the method, the sampling is carried out by a direct immersion extraction or headspace extraction technique [77]. Direct immersion could encounter difficulties with samples which contain a lot of impurities, compared to the headspace method. For both arrangements, the total extraction time is short and the method is easily automated. Desorption of the analytes depends on the analytical technique. In connection with GC, the desorption is performed directly in a specially modified liner in which a syringe-like device is placed and leads to good sensitivity thanks to quantitative transfer of the sample, rendering it a "green technology" because it is almost solvent-free. In other techniques, the analytes are mainly released into a suitable solvent. Unfortunately, this step can lead to sample dilution [7,79].

The silica fiber has many positive features and also drawbacks. The fiber is mechanically less resistant and also unstable in some organic solvents, the operating temperature cannot be very high because this would lead to the loss of analytes by thermal desorption and the extraction phase is not resistant and is removed during use. These facts led to a search for a different material which could form a fiber/wire and support the extraction phase (gold, stainless steel, platinum etc.) or to the development of new shapes which the extraction polymer could form [2]. Capillary tubes were developed with a film inside the open tube. The extraction surface is then larger so the extraction time can be shorter and the film is better protected [77]. In principle, there are no significant

TABLE 2 Summary of possible modifications of sorbent-based microextraction techniques

Modification	Commonly used abbreviation	Most common shape of the carrier of sorbent or sorbent itself	Selected review focused on the modification
Solid phase microextraction	SPME	fiber	Bojko et al. [7]; Souza Silva et al. [2]; Kumar et al. [80]
Microextraction by packed sorbent	MEPS	layer in the cartridge or syringe	Yang et al. [84]; Moein et al. [83]
Thin-film microextraction	TFME	thin film	Piri-Moghadam et al. [88]; Mirnaghi et al. [90]
Fabric phase sorptive extraction procedure	FPSE	flat sheet	Kabir et al. [94]
Stir bar sorptive extraction	SBSE	stir bar	Cardenas and Lucena [102]; He at al. [99]
Dispersive solid phase extraction	DSPE	micro- or nano-particles	Khezeli et al. [111]

differences in the arrangement in the fiber-based SPME methodology, but the main emphasis is placed on the development of new, modern, more selective, and efficient solid extraction phases (such as the sol-gel process, multi-walled carbon nanotubes, molecularly-imprinted polymers, etc.) that would be more durable [75]. This situation is summarized in a number of reviews [2,80,81], but will not be discussed further here, because it is beyond the scope of this review.

Several more methods could be included in the group of sorbent-based techniques. The use of packed sorbents similar to extraction cartridges in conventional solid phase extraction is one option. The system modified for microliter sample size is called the microextraction by packed sorbent method and was introduced in 2004 [82]. A wide range of sorbents mostly similar to those used in fiber-based techniques (C8, C18, porous graphic carbon, molecular imprinted polymers, etc.) are placed directly in the syringe barrel or in the narrowest part of an automatic pipette tip. The four-step process (conditioning of the extraction phase, sample loading, sample washing, and elution) can be fully automated. Because of the inclusion of an extraction phase regeneration step, the sorbents are reusable but particular attention must be paid to possible carry over [75,83,84]. The sample volumes required in this method are larger than for the fiber-based SPME. This method is suitable for the clinical or pharmacological applications (e.g. [85–87]).

The microextraction by packed sorbent method is time-consuming (sample preparation or clean-up step), requires a larger volume of sample, and is more expensive than fiber-based SPME. The drawbacks of both mentioned methods can be resolved by the use of new solid-phase extraction materials immobilized on a carrier that is differently shaped and additionally has other functions than just acting as a support material [88]. The extraction material can be applied as a thin film (thin-film microextraction), so the surface for the extraction is larger and consequently the sample volumes can be increased [89,90]. This method is very popular for non-invasive direct analysis of breath, skin or saliva [91,92]. The possibility of direct connection with MS is also a great advantage, specifically in direct analysis in real time (DART-MS/MS), where the extraction membrane is placed in the instrument without any previous desorption step [93]. Kabir et al. [94] described a new variant of thin-film microextraction and called it the fabric-phase sorptive extraction procedure, where they combined sol-gel coating technology with a cellulose fabric. The extraction material has a high sample capacity and the process is fast and it can be used for extraction of analytes from different samples (e.g. food [95], whole blood [96], urine or plasma [97]).

In 1999 a method was developed in which the extraction phase was immobilized directly on the stir bar and the method was called stir bar sorptive extraction [98]. The stir bar had two functions – to extract the analytes and to stir the solution to accelerate equilibration. The stirrer is then removed from the sample solution and the analytes are desorbed thermally or by a suitable organic solvent [99,100]. These stir bars are now commercial available. GERSTEL sells this device under the name Twister® or Twicester® for multi-stir bar sorptive extraction [101]. The shape of the stirrer can have one of two forms – stir membrane or stir disk [102].

Dispersive SPE is a new method that has been successfully used for a variety of preconcentration or extraction methods. It was introduced in 2003 by Anastassiades et al. [103]. The efficiency can be improved and the analysis time decreased using a method where free micro- or nanomaterials (particles with an extraction solid phase) are used as a solid phase. In this method, a micro or nano-material (particles) is added directly to the sample solution. Micro- and nanomaterials have two functions: first is the extraction of a target analyte from the sample solution and the second is dispersion of the solution, accelerating the extraction. The particles are then removed/isolated by centrifugation, filtration or magnetic nanoparticles can easily be isolated by a magnet [104]. The subsequent last step is desorption or elution of the analytes from the particle surface by an appropriate solvent. The main advantage, similar as for fiber-based SPME, is the availability

of new sorbents, which can be more selective [105,106]. The procedure is faster than fiber-based SPME and, in the case of nano-particles, there is no problem associated with high back pressure as for SPE cartridges. This technique is simple and does not require any special instrumentation. Overall, the technique seems to be very promising and researchers are focusing on the development of new nano-particles, especially magnetic ones [107,108] or another options could be magnetic carbon nanotube [109], quite cheap toner powder as magnetic sorbent [110] etc. All the new materials and types of sorbents for dispersive SPE, sometimes called micro-SPE, were summarized by Khezeli and Daneshfar [111].

4 | CONCLUDING REMARKS

Micro-extraction techniques are gradually being developed to achieve an ever-faster sample processing, less sample consumption, and higher measurement selectivity and sensitivity. This trend is also in line with the rapid development of micro-extraction procedures on the basis of single drop and sorbent-based techniques. The rapid development of this area raises the problem of non-uniform and inconsistent nomenclature, which makes it difficult to orientate within these methods. This review presented examples, applications, and evaluation of the microextraction techniques based on the distribution of analyzed substances between either single drop of extraction solvent and sample or sorbent and sample. The selected criteria applied are (a) the number of phases applied for the microextraction distinguishing two- and three-phase systems, (b) dynamics of the extraction process, i.e. dynamic and static, and (c) practical implementation of the technique, i.e. homogenous-phase, membrane-phase, single drop, and sorbent-based micro-extractions. The overlap of the criteria makes the method classification difficult, which is finally a result of the opinion and experience of the authors.

ACKNOWLEDGMENTS

The study was financially supported by the Charles University, project GA UK No 760216 and the project of the Specific University Research (SVV260440).

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

ORCID

Zuzana Bosakova http://orcid.org/0000-0002-8483-5739

REFERENCES

1. Arthur, C. L., Pawliszyn, J., Solid-phase microextraction with thermal-desorption using fused-silica optical fibers. *Anal. Chem.* 1990, *62*, 2145–2148.
2. Silva, E. A. S., Risticevic, S., Pawliszyn, J., Recent trends in SPME concerning sorbent materials, configurations and in vivo applications. *Trac-Trends Anal. Chem.* 2013, *43*, 24–36.
3. Jeannot, M. A., Cantwell, F. F., Solvent microextraction into a single drop. *Anal. Chem.* 1996, *68*, 2236–2240.
4. Liu, H. H., Dasgupta, P. K., Analytical chemistry in a drop. Solvent extraction in a microdrop. *Anal. Chem.* 1996, *68*, 1817–1821.
5. Lambropoulou, D. A., Albanis, T. A., Liquid-phase microextraction techniques in pesticide residue analysis. *J. Biochem. Biophys. Methods* 2007, *70*, 195–228.
6. Rezaee, M., Yamini, Y., Faraji, M., Evolution of dispersive liquid-liquid microextraction method. *J. Chromatogr. A* 2010, *1217*, 2342–2357.
7. Bojko, B., Cudjoe, E., Gomez-Rios, G. A., Gorynski, K., Jiang, R. F., Reyes-Garces, N., Risticevic, S., Silva, E. A. S., Togunde, O., Vuckovic, D., Pawliszyn, J., SPME - quo vadis? *Anal. Chim. Acta* 2012, *750*, 132–151.
8. Jeannot, M. A., Przyjazny, A., Kokosa, J. M., Single drop microextraction–development, applications and future trends. *J. Chromatogr. A* 2010, *1217*, 2326–2336.
9. He, Y., Lee, H. K., Liquid phase microextraction in a single drop of organic solvent by using a conventional microsyringe. *Anal. Chem.* 1997, *69*, 4634–4640.
10. Kokosa, J. M., Recent trends in using single-drop microextraction and related techniques in green analytical methods. *Trac-Trends Anal. Chem.* 2015, *71*, 194–204.
11. Deng, C. H., Yao, N., Wang, B., Zhang, X. M., Development of microwave-assisted extraction followed by headspace single-drop microextraction for fast determination of paeonol in traditional Chinese medicines. *J. Chromatogr. A* 2006, *1103*, 15–21.
12. Liu, W. P., Lee, H. K., Continuous-flow microextraction exceeding1000-fold concentration of dilute analytes. *Anal. Chem.* 2000, *72*, 4462–4467.
13. Wu, H. F., Yen, J. H., Chin, C. C., Combining drop-to-drop solvent microextraction with gas chromatography/mass spectrometry using electronic ionization and self-ion/molecule reaction method to determine methoxyacetophenone isomers in one drop of water. *Anal. Chem.* 2006, *78*, 1707–1712.
14. Lu, Y. C., Lin, Q., Luo, G. S., Dai, Y. Y., Directly suspended droplet microextraction. *Anal. Chim. Acta* 2006, *566*, 259–264.
15. Zanjani, M. R. K., Yamini, Y., Shariati, S., Jonsson, J. A., A new liquid-phase microextraction method based on solidification of floating organic drop. *Anal. Chim. Acta* 2007, *585*, 286–293.
16. Theis, A. L., Waldack, A. J., Hansen, S. M., Jeannot, M. A., Headspace solvent microextraction. *Anal. Chem.* 2001, *73*, 5651–5654.
17. Sarafraz-Yazdi, A., Beiknejad, D., Es'haghi, Z., LC determination of mono-substituted phenols in water using liquid-liquid-liquid phase microextraction. *Chromatographia* 2005, *62*, 49–54.

18. Sarafraz-Yazdi, A., Mofazzeli, F., Es'haghi, Z., Directly suspended droplet three liquid phase microextraction of diclofenac prior to LC. *Chromatographia* 2008, *67*, 49–53.
19. Jeannot, M. A., Cantwell, F. F., Mass transfer characteristics of solvent extraction into a single drop at the tip of a syringe needle. *Anal. Chem.* 1997, *69*, 235–239.
20. Yao, C., Pitner, W. R., Anderson, J. L., Ionic liquids containing the tris(pentafluoroethyl)trifluorophosphate anion: a new class of highly selective and ultra hydrophobic solvents for the extraction of polycyclic aromatic hydrocarbons using single drop microextraction. *Anal. Chem.* 2009, *81*, 5054–5063.
21. Clark, K. D., Emaus, M. N., Varona, M., Bowers, A. N., Anderson, J. L., Ionic liquids: solvents and sorbents in sample preparation. *J. Sep. Sci.* 2018, *41*, 209–235.
22. Aguilera-Heirador, E., Lucena, R., Cardenas, S., Valcarcel, M., Direct coupling of ionic liquid based single-drop microextraction and GC/MS. *Anal. Chem.* 2008, *80*, 793–800.
23. Ruiz-Palomero, C., Soriano, M. L., Valcarcel, M., Ternary composites of nanocellulose, carbonanotubes and ionic liquids as new extractants for direct immersion single drop microextraction. *Talanta* 2014, *125*, 72–77.
24. Wen, X. D., Deng, Q. W., Wang, J. W., Yang, S. C., Zhao, X., A new coupling of ionic liquid based-single drop microextraction with tungsten coil electrothermal atomic absorption spectrometry. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 2013, *105*, 320–325.
25. Cabala, R., Bursova, M., Bell-shaped extraction device assisted liquid-liquid microextraction technique and its optimization using response-surface methodology. *J. Chromatogr. A* 2012, *1230*, 24–29.
26. Ouyang, G. F., Zhao, W. N., Pawliszyn, J., Automation and optimization of liquid-phase microextraction by gas chromatography. *J. Chromatogr. A* 2007, *1138*, 47–54.
27. Williams, D. B. G., George, M. J., Meyer, R., Marjanoyic, L., Bubbles in solvent microextraction: the influence of intentionally introduced bubbles on extraction efficiency. *Anal. Chem.* 2011, *83*, 6713–6716.
28. Williams, D. B. G., George, M. J., Marjanovic, L., Rapid detection of atrazine and metolachlor in farm soils: gas chromatography-mass spectrometry-based analysis using the bubble-in-drop single drop microextraction enrichment method. *J. Agric. Food Chem.* 2014, *62*, 7676–7681.
29. Wang, X. W., Yuan, K., Liu, H. T., Lin, L., Luan, T. G., Fully automatic exposed and in-syringe dynamic single-drop microextraction with online agitation for the determination of polycyclic musks in surface waters of the pearl river estuary and south china sea. *J. Sep. Sci.* 2014, *37*, 1842–1849.
30. Shrivas, K., Wu, H. F., Rapid determination of caffeine in one drop of beverages and foods using drop-to-drop solvent microextraction with gas chromatography/mass spectrometry. *J. Chromatogr. A* 2007, *1170*, 9–14.
31. Shrivas, K., Patel, D. K., Matrix-assisted laser desorption/ionization mass spectrometry for quantitative determination of beta-blocker drugs in one-drop of human serum sample. *J. Chromatogr. B* 2011, *879*, 35–40.
32. Shrivas, K., Wu, H. F., Quantitative bioanalysis of quinine by atmospheric pressure-matrix assisted laser desorption/ionization mass spectrometry combined with dynamic drop-to-drop solvent microextraction. *Anal. Chim. Acta* 2007, *605*, 153–158.
33. Zhang, M. S., Huang, J. R., Zeng, J. B., Yu, J. F., Ultrasonic-assisted drop-to-drop solvent microextraction in a capillary tube coupled with GC-FID for trace analysis of phthalate esters. *J. Chromatogr. Sci.* 2014, *52*, 739–744.
34. Vidal, L., Chisvert, A., Canals, A., Salvador, A., Ionic liquid-based single-drop microextraction followed by liquid chromatography-ultraviolet spectrophotometry detection to determine typical UV filters in surface water samples. *Talanta* 2010, *81*, 549–555.
35. Liu, Y., Hashi, Y., Lin, J. M., Continuous-flow microextraction and gas chromatographic-mass spectrometric determination of polycyclic aromatic hydrocarbon compounds in water. *Anal. Chim. Acta* 2007, *585*, 294–299.
36. Liu, S. R., Dasgupta, P. K., Liquid droplet–a renewable gas sampling interface. *Anal. Chem.* 1995, *67*, 2042–2049.
37. Mahugo-Santana, C., Sosa-Ferrera, Z., Torres-Padron, M. E., Santana-Rodriguez, J. J., Application of new approaches to liquid-phase microextraction for the determination of emerging pollutants. *Trac-Trends Anal. Chem.* 2011, *30*, 731–748.
38. Jain, A., Verma, K. K., Recent advances in applications of single-drop microextraction: a review. *Anal. Chim. Acta* 2011, *706*, 37–65.
39. Farajzadeh, M. A., Khoshmarram, L., Sheykhizadeh, S., A review on application of microextraction techniques for analysis of chemical compounds and metal ions in foodstuffs. *Anal. Bioanal. Chem. Res.* 2014, *1*, 1–19.
40. Pytlakowska, K., Energy-dispersive X-ray spectrometry combined with directly suspended droplet microextraction for determination of dissolved silicate in surface water via silicomolybdenum blue complex. *Talanta* 2014, *128*, 480–485.
41. Wang, Y. Y., Zhao, G. Y., Chang, Q. Y., Zang, X. H., Wang, C., Wang, Z., Developments in solidification of floating organic drop liquid phase microextraction. *Chinese J. Anal. Chem.* 2010, *38*, 1517–1522.
42. Ghambarian, M., Yamini, Y., Esrafili, A., Liquid-phase microextraction based on solidified floating drops of organic solvents. *Microchim. Acta* 2013, *180*, 519–535.
43. Ganjali, M. R., Sobhi, H. R., Farahani, H., Norouzi, P., Dinarvand, R., Kashtiaray, A., Solid drop based liquid-phase microextraction. *J. Chromatogr. A* 2010, *1217*, 2337–2341.
44. Guo, X. Q., He, M., Chen, B. B., Hu, B., Solidified floating organic drop microextraction combined with ETV-ICP-MS for the determination of trace heavy metals in environmental water samples. *Talanta* 2012, *94*, 70–76.
45. Pelit, F. O., Yengin, C., Application of solidified floating organic drop microextraction method for biomonitoring of chlorpyrifos and its oxon metabolite in urine samples. *J. Chromatogr. B* 2014, *949*, 109–114.
46. Tankeviciute, A., Kazlauskas, R., Vickackaite, V., Headspace extraction of alcohols into a single drop. *Analyst* 2001, *126*, 1674–1677.
47. Lee, H. R., Cho, S. M., Kim, J., Chung, D. S., Novel and simple headspace in-tube microextraction coupled with capillary electrophoresis. *J. Chromatogr. A* 2014, *1346*, 117–122.

48. Ouyang, G. F., Zhao, W. N., Pawliszyn, J., Kinetic calibration for automated headspace liquid-phase microextraction. *Anal. Chem.* 2005, *77*, 8122–8128.

49. Chen, Y., Li, Y., Xiong, Y. Q., Fang, C. C., Wang, X. T., An effective pre-treatment method for the determination of short-chain fatty acids in a complex matrix by derivatization coupled with headspace single-drop microextraction. *J. Chromatogr. A* 2014, *1325*, 49–55.

50. Farajzadeh, M. A., Nouri, N., Khorram, P., Derivatization and microextraction methods for determination of organic compounds by gas chromatography. *Trac-Trends Anal. Chem.* 2014, *55*, 14–23.

51. Kokosa, J. M., Advances in solvent-microextraction techniques. *Trac-Trends Anal. Chem.* 2013, *43*, 2–13.

52. Gao, W. H., Chen, G. P., Chen, T. F., Zhang, X. S., Chen, Y. W., Hu, Z. D., Directly suspended droplet microextraction combined with single drop back-extraction as a new approach for sample preparation compatible with capillary electrophoresis. *Talanta* 2011, *83*, 1673–1679.

53. Ma, M. H., Cantwell, F. F., Solvent microextraction with simultaneous back-extraction for sample cleanup and preconcentration: quantitative extraction. *Anal. Chem.* 1998, *70*, 3912–3919.

54. Ma, M. H., Cantwell, F. F., Solvent microextraction with simultaneous back-extraction for sample cleanup and preconcentration: preconcentration into a single microdrop. *Anal. Chem.* 1999, *71*, 388–393.

55. Zhao, L. M., Lee, H. K., Determination of phenols in water using liquid phase microextraction with back extraction combined with high-performance liquid chromatography. *J. Chromatogr. A* 2001, *931*, 95–105.

56. He, Y., Kang, Y. J., Single drop liquid-liquid-liquid microextraction of methamphetamine and amphetamine in urine. *J. Chromatogr. A* 2006, *1133*, 35–40.

57. Sarafra-Yazdi, A., Es'haghi, Z., Antibiotic-assisted three-phase liquid-phase microextraction of aromatic amines from aqueous solutions combined with high-performance liquid chromatography. *J. Anal. Chem.* 2006, *61*, 787–793.

58. Sarafraz-Yazdi, A., Mofazzeli, F., Es'haghi, Z., Determination of chlorophenols in environmental water samples using directly suspended droplet liquid-liquid-liquid phase microextraction prior to high-performance liquid chromatography. *Int. J. Environ. Anal. Chem.* 2010, *90*, 1108–1118.

59. Yazdi, A. S., Mofazzeli, F., Es'haghi, Z., Determination of 3-nitroaniline in water samples by directly suspended droplet three-phase liquid-phase microextraction using 18-crown-6 ether and high-performance liquid chromatography. *J. Chromatogr. A* 2009, *1216*, 5086–5091.

60. Farahani, H., Norouzi, P., Beheshti, A., Sobhi, H. R., Dinarvand, R., Ganjali, M. R., Quantitation of atorvastatin in human plasma using directly suspended acceptor droplet in liquid-liquid-liquid microextraction and high-performance liquid chromatography-ultraviolet detection. *Talanta* 2009, *80*, 1001–1006.

61. Zhang, Y. F., Lee, H. K., Liquid phase microextraction using knitting wool as the extractant phase holder before chromatographic analysis: a new approach for trace analysis. *J. Chromatogr. A* 2013, *1273*, 12–17.

62. Saraji, M., Farajmand, B., Microporous silica with nanolayer structure coated with renewable organic solvent film as a novel extracting phase: a combination of solid- and liquid-phase microextraction. *Anal. Chim. Acta* 2012, *721*, 61–67.

63. Ho, T. T., Chen, C. Y., Li, Z. G., Yang, T. C. C., Lee, M. R., Determination of chlorophenols in landfill leachate using headspace sampling with ionic liquid-coated solid-phase microextraction fibers combined with gas chromatography-mass spectrometry. *Anal. Chim. Acta* 2012, *712*, 72–77.

64. Kocurova, L., Balogh, I. S., Andruch, V., Solvent microextraction: a review of recent efforts at automation. *Microchem J.* 2013, *110*, 599–607.

65. Spietelun, A., Marcinkowski, L., de la Guardia, M., Namiesnik, J., Green aspects, developments and perspectives of liquid phase microextraction techniques. *Talanta* 2014, *119*, 34–45.

66. Xu, L., Basheer, C., Lee, H. K., Developments in single-drop microextraction. *J. Chromatogr. A* 2007, *1152*, 184–192.

67. Sarafraz-Yazdi, A., Amiri, A., Liquid-phase microextraction. *Trac-Trends Anal. Chem.* 2010, *29*, 1–14.

68. Santana-Rodriguez, J. J., Mahugo-Santana, C., Sosa-Ferrera, Z., Torres-Padron, M. E., Application of new approaches to liquid-phase microextraction for the determination of emerging pollutants. *Trac-Trend Anal. Chem.* 2011, *30*, 731–748.

69. Pakade, Y. B., Tewary, D. K., Development and applications of single-drop microextraction for pesticide residue analysis: a review. *J. Sep. Sci.* 2010, *33*, 3683–3691.

70. Kataoka, H., Recent developments and applications of microextraction techniques in drug analysis. *Anal. Bioanal. Chem.* 2010, *396*, 339–364.

71. Mirmoghaddam, M., Kaykhaii, M., Yahyavi, H., Recent developments in the determination of residual solvents in pharmaceutical products by microextraction methods. *Anal. Methods* 2015, *7*, 8511–8523.

72. Pena-Pereira, F., Lavilla, I., Bendicho, C., Miniaturized preconcentration methods based on liquid-liquid extraction and their application in inorganic ultratrace analysis and speciation: a review. *Spectrochim. Acta B* 2009, *64*, 1–15.

73. Yan, Y. Y., Chen, X., Hu, S., Bai, X. H., Applications of liquid-phase microextraction techniques in natural product analysis: a review. *J. Chromatogr. A* 2014, *1368*, 1–17.

74. Callejon, R. M., Ubeda, C., Rios-Reina, R., Morales, M. L., Troncoso, A. M., Recent developments in the analysis of musty odour compounds in water and wine: a review. *J. Chromatogr. A* 2016, *1428*, 72–85.

75. Ocana-Gonzalez, J. A., Fernandez-Torres, R., Bello-Lopez, M. A., Ramos-Payan, M., New developments in microextraction techniques in bioanalysis. A review. *Anal. Chim. Acta* 2016, *905*, 8–23.

76. Vičkačkaitė, V., Padarauskas, A., Ionic liquids in microextraction techniques. *Cent. Eur. J. Chem.* 2012, *10*, 652–674.

77. Kabir, A., Locatelli, M., Ulusoy, H. I., Recent trends in microextraction techniques employed in analytical and bioanalytical sample preparation. *Separations* 2017, *4*, 1–15.

78. Malik, A. K., Kaur, V., Verma, N., A review on solid phase microextraction - high performance liquid chromatography as a

novel tool for the analysis of toxic metal ions. *Talanta* 2006, *68*, 842–849.

79. Zhang, Z., Yang, M. J., Pawliszyn, J., Solid-phase microextraction. A solvent-free alternative for sample preparation. *Anal. Chem.* 1994, *66*, 844A-853A.
80. Kumar, A., Gaurav, M. A. K., Tewary, D. K., Singh, B., A review on development of solid phase microextraction fibers by sol-gel methods and their applications. *Anal. Chim. Acta* 2008, *610*, 1–14.
81. Spietelun, A., Marcinkowski, L., de la Guardia, M., Namiesnik, J., Recent developments and future trends in solid phase microextraction techniques towards green analytical chemistry. *J. Chromatogr. A* 2013, *1321*, 1–13.
82. Abdel-Rehim, M., New trend in sample preparation: on-line microextraction in packed syringe for liquid and gas chromatography applications - I. Determination of local anaesthetics in human plasma samples using gas chromatography-mass spectrometry. *J. Chromatogr. B* 2004, *801*, 317–321.
83. Moein, M. M., Abdel-Rehim, A., Abdel-Rehim, M., Microextraction by packed sorbent (MEPS). *Trac-Trends Anal. Chem.* 2015, *67*, 34–44.
84. Yang, L., Said, R., Abdel-Rehim, M., Sorbent, device, matrix and application in microextraction by packed sorbent (MEPS): a review. *J. Chromatogr. B* 2017, *1043*, 33–43.
85. D'Angelo, V., Tessari, F., Bellagamba, G., De Luca, E., Cifelli, R., Celia, C., Primavera, R., Di Francesco, M., Paolino, D., Di Marzio, L., Locatelli, M., Microextraction by packed sorbent and HPLC-PDA quantification of multiple anti-inflammatory drugs and fluoroquinolones in human plasma and urine. *J. Enzym Inhib.* 2016, *31*, 110–116.
86. Locatelli, M., Ciavarella, M. T., Paolino, D., Celia, C., Fiscarelli, E., Ricciotti, G., Pompilio, A., Di Bonaventura, G., Grande, R., Zengin, G., Di Marzio, L., Determination of ciprofloxacin and levofloxacin in human sputum collected from cystic fibrosis patients using microextraction by packed sorbent-high performance liquid chromatography photodiode array detector. *J. Chromatogr. A* 2015, *1419*, 58–66.
87. Locatelli, M., Ferrone, V., Cifelli, R., Barbacane, R. C., Carlucci, G., Microextraction by packed sorbent and high performance liquid chromatography determination of seven non-steroidal anti-inflammatory drugs in human plasma and urine. *J. Chromatogr. A* 2014, *1367*, 1–8.
88. Piri-Moghadam, H., Alam, M. N., Pawliszyn, J., Review of geometries and coating materials in solid phase microextraction: opportunities, limitations, and future perspectives. *Anal. Chim. Acta* 2017, *984*, 42–65.
89. Bruheim, I., Liu, X. C., Pawliszyn, J., Thin-film microextraction. *Anal. Chem.* 2003, *75*, 1002–1010.
90. Mirnaghi, F. S., Hein, D., Pawliszyn, J., Thin-film microextraction coupled with mass spectrometry and liquid chromatography-mass spectrometry. *Chromatographia* 2013, *76*, 1215–1223.
91. Zhou, J. M., Huang, Z. A., Kumar, U., Chen, D. D. Y., Review of recent developments in determining volatile organic compounds in exhaled breath as biomarkers for lung cancer diagnosis. *Anal. Chim. Acta* 2017, *996*, 1–9.
92. Lawal, O., Ahmed, W. M., Nijsen, T. M. E., Goodacre, R., Fowler, S. J., Exhaled breath analysis: a review of 'breath-taking' methods for off-line analysis. *Metabolomics* 2017, *13*, 16.
93. Rodriguez-Lafuente, A., Mirnaghi, F. S., Pawliszyn, J., Determination of cocaine and methadone in urine samples by thin-film solid-phase microextraction and direct analysis in real time (DART) coupled with tandem mass spectrometry. *Anal. Bioanal. Chem.* 2013, *405*, 9723–9727.
94. Kabir, A., Mesa, R., Jurmain, J., Furton, K. G., Fabric phase sorptive extraction explained. *Separations* 2017, *4*, 21.
95. Samanidou, V., Filippou, O., Marinou, E., Kabir, A., Furton, K. G., Sol-gel-graphene-based fabric-phase sorptive extraction for cow and human breast milk sample cleanup for screening bisphenol a and residual dental restorative material before analysis by HPLC with diode array detection. *J. Sep. Sci.* 2017, *40*, 2612–2619.
96. Locatelli, M., Tinari, N., Grassadonia, A., Tartaglia, A., Macerola, D., Piccolantonio, S., Sperandio, E., D'Ovidio, C., Carradori, S., Ulusoy, H. I., Furton, K. G., Kabir, A., FPSE-HPLC-DAD method for the quantification of anticancer drugs in human whole blood, plasma, and urine. *J. Chromatogr. B* 2018, *1095*, 204–213.
97. Locatelli, M., Kabir, A., Innosa, D., Lopatriello, T., Furton, K. G., A fabric phase sorptive extraction-high performance liquid chromatography-photo diode array detection method for the determination of twelve azole antimicrobial drug residues in human plasma and urine. *J. Chromatogr. B* 2017, *1040*, 192–198.
98. Baltussen, E., Sandra, P., David, F., Cramers, C., Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: theory and principles. *J. Microcolumn Sep.* 1999, *11*, 737–747.
99. He, M., Chen, B. B., Hu, B., Recent developments in stir bar sorptive extraction. *Anal. Bioanal. Chem.* 2014, *406*, 2001–2026.
100. Kawaguchi, M., Ito, R., Saito, K., Nakazawa, H., Novel stir bar sorptive extraction methods for environmental and biomedical analysis. *J. Pharm. Biomed. Anal.* 2006, *40*, 500–508.
101. GERSTEL http://www.gerstel.com/en/twister-stir-bar-sorptive-extraction.htm (last time accessed: April 20, 2018).
102. Cardenas, S., Lucena, R., Recent advances in extraction and stirring integrated techniques. *Separations* 2017, *4*, 16.
103. Anastassiades, M., Lehotay, S. J., Stajnbaher, D., Schenck, F. J., Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *J. AOAC Int.* 2003, *86*, 412–431.
104. Mehdinia, A., Khojasteh, E., Kayyal, T. B., Jabbari, A., Magnetic solid phase extraction using gold immobilized magnetic mesoporous silica nanoparticles coupled with dispersive liquid-liquid microextraction for determination of polycyclic aromatic hydrocarbons. *J. Chromatogr. A* 2014, *1364*, 20–27.
105. Contin, M., Flor, S., Martinefski, M., Lucangioli, S., Tripodi, V., The use of coenzyme Q0 as a template in the development of a molecularly imprinted polymer for the selective recognition of coenzyme Q10. *Anal. Chim. Acta* 2014, *807*, 67–74.
106. Yan, H. Y., Wang, H., Qiao, J. D., Yang, G. L., Molecularly imprinted matrix solid-phase dispersion combined with dispersive

liquid-liquid microextraction for the determination of four sudan dyes in egg yolk. *J. Chromatogr. A* 2011, *1218*, 2182–2188.

107. Yavuz, E., Tokalioglu, S., Patat, S., Magnetic dispersive solid phase extraction with graphene/$ZnFe_2O_4$ nanocomposite adsorbent for the sensitive determination of mercury in water and fish samples by cold vapor atomic absorption spectrometry. *Microchem. J.* 2018, *142*, 85–93.
108. Socas-Rodriguez, B., Hernandez-Borges, J., Herrera-Herrera, A. V., Rodriguez-Delgado, M. A., Multiresidue analysis of oestrogenic compounds in cow, goat, sheep and human milk using core-shell polydopamine coated magnetic nanoparticles as extraction sorbent in micro-dispersive solid-phase extraction followed by ultra-high-performance liquid chromatography tandem mass spectrometry. *Anal. Bioanal. Chem.* 2018, *410*, 2031–2042.
109. Pastor-Belda, M., Marin-Soler, L., Campillo, N., Vinas, P., Hernandez-Cordoba, M., Magnetic carbon nanotube composite for the preconcentration of parabens from water and urine samples using dispersive solid phase extraction. *J. Chromatogr. A* 2018, *1564*, 102–109.
110. Farajzadeh, M. A., Mohebbi, A., Development of magnetic dispersive solid phase extraction using toner powder as an efficient and economic sorbent in combination with dispersive liquid-liquid microextraction for extraction of some widely used pesticides in fruit juices. *J. Chromatogr. A* 2018, *1532*, 10–19.
111. Khezeli, T., Daneshfar, A., Development of dispersive micro-solid phase extraction based on micro and nano sorbents. *Trac-Trends Anal. Chem.* 2017, *89*, 99–118.

How to cite this article: Havlikova M, Cabala R, Pacakova V, Bursova M, Bosakova Z. Critical evaluation of microextraction pretreatment techniques – Part 1: Single drop and sorbent-based techniques. *J Sep Sci* 2019;42:273–284. https://doi.org/10.1002/jssc.201800902