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Ultrasonic and Cooling Approaches for Reinforcement of the Microextraction Methods

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Since solvent-free methods of solid-phase and liquid-phase microextraction (SPME and LPME) were introduced, many efforts have been made to improve their modes and applications. However, due to limitations with sensitivity and efficiency, researchers have focused on improving the performance of their basic primary modes. In this respect, in recent years, different methods such as ultrasonic-assisted microextraction (UA-ME), microwave-assisted microextraction (MA-ME), solvent-assisted microextraction (SA-ME), salt-assisted microextraction, surfactant-assisted microextraction and cooling-assisted microextraction (CA-ME) have been developed to reinforce the efficiency of the SPME and LPME methods. These strategies make the microextraction methods more effective and applicable for different sample matrices. In this article, UA-ME and CA-ME, as the most important methods to enhance the efficiency of SPME and LPME, were reviewed and their different aspects were evaluated and compared, from 1989 to 2016. Comparison of different microextraction reinforcement approaches revealed that CA-ME is the most effective method to increase the extraction efficiency, especially for the analysis of complicated solid matrices.

Keywords: Ultrasonic-assisted microextraction, Cooling-assisted microextraction, Solid-phase microextraction, Liquid-phase microextraction

INTRODUCTION

Due to disadvantages of the classical extraction methods, solid-phase extraction (SPE) was introduced as an effective alternative to compensate these limitations [1]. After a while, scientists thought to rectify the defects of SPE using the sample extraction by an optical fiber and its direct introduction into the gas chromatograph (GC) injector, followed by laser desorption [2]. This method reduced using of organic solvents, but needed involute instrumental reform of the GC system. A clever idea for solving this problem was the implementation of a coated fused silica fiber on plunger's tip of a microsyringe followed by its introduction into the GC injector for thermal desorption [3], so SPME was introduced [4]. SPME reduced the steps and time of analytical analyses and opened up a new horizon for analysts.

For more than two decades since introducing of SPME [5] many efforts have been made to improve its different aspects [6,7]. However, due to complications of the practical manipulation, very few researchers have focused on improving the performance of its basic primary modes [8]. Additionally, the proposed designs and developments not only were expensive and complicated, but also could not significantly improve the abilities and extraction efficiency of SPME. Consequently, LPME was introduced [9] and followed by publication of extensive research for its development [10-12]. Recently, different approaches have been developed to reinforce the efficiency of the SPME and LPME methods, such as ultrasonic-assisted microextraction (UA-ME), microwave-assisted microextraction (MA-ME), salt-assisted microextraction, solvent-assisted

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microextraction (SA-ME), surfactant-assisted microextraction and cooling-assisted microextraction (CA-ME). Among the few succeeded endeavors made to raise the efficiency of the microextraction methods, (UA-ME) [13,14] and CA-ME [15,16] were demonstrated to be more efficient. UA-ME and CA-ME are very efficient and reliable, especially in complicated matrices such as soil, sludge and clay, with analytes tightly attached to their active sites.

Ultrasonic irradiation is a well-known and widespread technique to accelerate various steps of an analytical process. This type of energy is of great help in pretreatment of solid and liquid samples, as it facilitates and accelerates operations such as the extraction of target analytes [17], slurry dispersion [18], emulsification [19], homogenization [20], nebulization [21], washing [22], derivatization [23,24] and especially cloudy media formation in dispersive liquid-liquid microextraction (DLLME) [25,26]. Ultrasound-assisted extraction (UAE) is an effective strategy to release analytes from different types of samples. The influence of highly effective temperatures, developing the solubility and diffusivity, and pressures, favoring penetration and transport, at the interface between an aqueous or organic solution subjected to ultrasonic energy and a solid matrix, in addition to the oxidative energy of radicals created during sonolysis of the solvent, result in a high extractive power [13]. UAE as an accelerator is a low-cost and efficient alternative to conventional extraction methods and, in some cases, even to microwave-assisted extraction (MAE), as used in different analytes in a wide variety of sample matrices [27].

A serious challenge in environmental, biological and food solid matrices is extracting and trapping volatile organic compounds (VOCs). Direct thermal desorption (DTD) [28], static headspace sampling (SHS) [29], headspace sorptive extraction (HSSE) [30], and headspace solid-phase microextraction (HS-SPME) [6] are some general alternatives to the conventional extraction methods for VOCs. However, to select a proper method, different variables including matrix complexity, physicochemical characteristics and amount of analytes in the sample should be considered [31]. HS-SPME is not as sensitive as DTD, but has a better sensitivity than SHS. Thus, for effective extraction of volatiles from solid matrices, improving the sensitivity of HS-SPME is a major concern [32]. The main challenges in HS-SPME are releasing low volatile analytes from their native matrix into the headspace and collecting them onto the microextraction phase, especially in complicated solid matrices. The most effective solution to release analytes from their matrix is thermal desorption, which provides enough kinetic energy and reinforces molecules to escape from their matrix, enhances the mass transfer to pass through the sample tissue, and increases their concentration in the headspace. However, due to exothermic character of sorption, increasing temperature of the sample can conversely decrease trapping analytes onto the fiber's coating. Indeed, temperature has a bilateral effect. It increases the extraction efficiency by increasing concentration in headspace, in one hand, and decreases the tendency of the coating to trap the analytes, on the other hand. Therefore, in temperature profile of each HS-SPME sampling method, there is usually an optimum temperature [15], which is not usually high enough for significant improvement of the extraction efficiency of volatiles, especially in solid matrices with their analytes firmly attached. This effect may be compensated by creating a temperature gap between the fiber and headspace, to simultaneously increase the distribution coefficients of equilibriums between the sample matrix and headspace as well as between the headspace and fiber. Practically, this means heating the sample matrix to high temperatures and concurrently cooling the fiber at low temperatures [8]. This strategy allows the contaminated samples, such as soils and sediments, to be directly analyzed with minimal sample manipulation.

In this review study, the published UA-ME and CA-ME methods, are briefly described, as a simple and reliable monothetic classification system. Different important aspects of these systems, such as fabrication techniques, extraction procedures, applications, and performances are discussed. Additionally, the efficiency of different cooling systems such as thermoelectric coolers (TECs) and cryogenic coolers are discussed. Finally, on the basis of the present results, some proper suggestions are offered for

further extension and improvement of these methods.

ULTASONIC-ASSISTED MICROEXTRACTION (UA-ME)

Ultrasonic-Assisted Solid-phase Microextraction (UA-SPME)

The use of sonication in the SPME procedure has been reported by different authors to increase the release and pass of VOCs to the headspace and reduce the extraction time [33,34], or to facilitate desorption of the compounds collected onto the fiber [35]. Rial-Otero *et al.* [36] reported a UA-SPME method for simultaneous extraction of acaricides in honey samples followed by gas chromatography-mass spectrometry (GC-MS) determination. The use of sonication during the SPME extraction has increased the recoveries when compared with extraction using magnetic stirring. In addition, the extraction time was reduced *ca*. 25%. In a similar research, the UA-HS-SPME strategy was applied for the extraction of VOCs from *Carum carvi* L. medicinal plant [37]. UAE has been also utilized in other configurations of SPME such as matrix solid-phase dispersion (MSPD) [38] and solvent bar microextraction (SBME) [39].

Ultrasonic-Assisted Liquid-phase Microextraction (UA-LPME)

High ability of ultrasonic irradiation in dispersion of solvents in DLLME procedure has made it an advantageous microextraction technique. DLLME is based on a ternary component solvent system like homogeneous liquid-liquid extraction (HLLE) and cloud point extraction (CPE), in which an appropriate mixture of extracting and dispersing solvents is injected rapidly into an aqueous sample by a syringe, and then a cloudy solution is formed. Formation of the cloudy media remarkably increases the contact surface between the phases and reduces the extraction time and also increases the enrichment factor [40]. However, it still has some limitations, including low repeatability, difficulty to be automated and low enrichment factor (caused by using large amounts of disperser solvent). Therefore, an ultrasonic dispersion process can be applied to accelerate the formation of the fine cloudy solution without using dispersing solvents, which significantly increases the extraction efficiency and reduces the equilibrium time [41,42]. This innovation has been used in a wide range of research activities, such as analysis of nitric oxide produced in PC12 cells [43], phthalate esters in bottled water [44], imidacloprid in tomato [41], pyrethroids in river water [45], chromium(VI) in water samples [46], ursolic acid in force loquat capsule [47], biogenic amines in beer [48], essential oil of *Oliveria decumbens* Vent [49] copper, nickel and lead in food samples [26], propoxur in environmental and beverage samples [50], heavy metals in real water samples [19], aluminum in drinking water, blood and urine samples of kidney failure patients [51] and orange peel metabolites [52]. Ultrasonic irradiation has been also used in emulsification in the solidified floating organic drop microextraction (SFODME) method [53,54]. Schematic representation of an ultrasound-assisted emulsification microextraction (UA-EME) method, based on applying low density organic solvents [55], is shown in Fig. 1.

Ultrasonic Nebulization Extraction Headspace Single-drop Microextraction (UNE-HS-SDME)

Ultrasonic nebulization extraction (UNE) was first introduced in 2005 [56]. The frequency of ultrasonic vibration is about 1.7 MHz in the UNE process. When the vibration is transmitted through the solvent, an "ultrasonic fountain" occurs leading to a rapid gas-liquid distribution equilibrium of analyte So, if the analyte has a good volatility, equilibrium concentration of the vapor phase will be achieved after completion of the UNE process. Additionally, the UNE is beneficial to compounds which are sensitive to temperature, because extraction temperature is low in this process [57,58]. UNE, coupled with the HS-SDME sampling method (Fig. 2), has been applied for analysis of essential oil in *Cuminum cyminum* L. [56], volatile compounds in *Forsythia suspensa* [59] and volatiles in the pericarp of *Zanthoxylum bungeanum Maxim* [60]. It was also coupled with headspace hollow-fiber liquid-phase microextraction (HS-HF-LPME) and used for analysis of pesticides from root of *Panax* ginseng C.A. Mey [61]. In an another research, UNE was coupled to a DLLME strategy and utilized for sampling of parabens in cosmetic products followed by gas chromatography-flame ionization detection (GC-FID) determination [21]. Different analytical aspects of the studied UA-ME methods are summarized in Table 1.

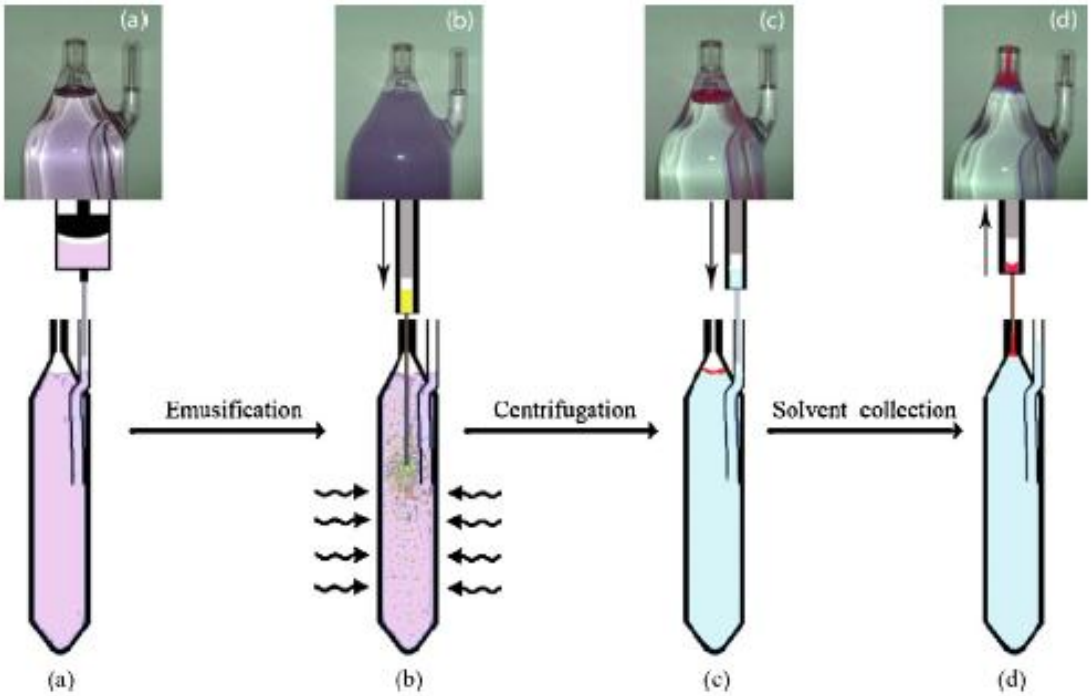

Fig. 1. Schematic of UA-EME applying low density organic solvent, (a) aqueous sample solution in the home-designed emulsification glass vial, (b) simultaneous injection and emulsification of 14 µl toluene into aqueous sample, (c) addition of a few µl of doubly distilled water into the vial and (d) collection of toluene transferred into the capillary tube at the top of the vial (4 µl) [56].

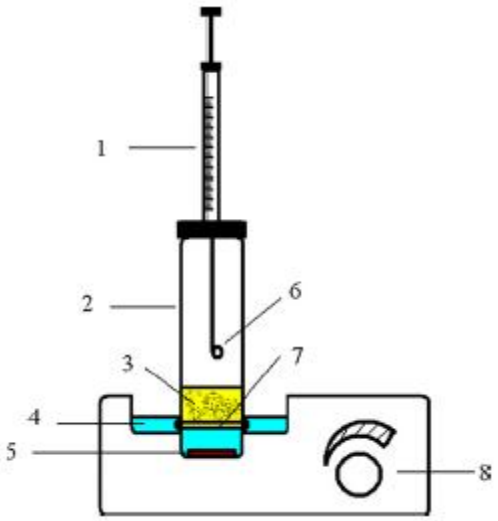

Fig. 2. UNE-HS-SDME system, 1) microsyringe, 2) extraction vessel, 3) sample powder and extraction solvent, 4) coupling water, 5) piezocrystal, 6) microdrop, 7) PVC film, and 8) power controller [57].

Table 1. Different Analytical Aspects of the Studied UA-ME Methods, which have been Reported in the Literature

Technique	Analyte	Sonication time	LOD	Extraction phase	Sample	Detection	Ref.
a) Ultrasonic-Assisted Solid-Phase Microextraction (UA-SPME)							
UA-HS-SPME	Dimethyl disulfide	30 min	25 μg l^{-1}	PDMS fiber	Fermented vegetable	GC-FID	[33]
UA-HS-SPME	Residual styrene monomer	15 min	-	CAR/PDMS fiber	Expanded polystyrene (EPS)	GC-MS	[34]
UA-DI-SPME	Isocyanate	90 S for desorption	3.2 μg m^{-3}	Dibutylamine loaded onto PDMS/DVB fiber	Atmosphere	LC-MS	[35]
UA-HS-SPME	Acaricides	30 min	15 ng g^{-1}	PA fiber	Honey	GC-MS	[36]
UA-HS-SPME	Essential oil constituents	15 min	-	PDMS fiber	Carum carvi L	GC-MS	[37]
US-MMSPD coupled HLLE	Organochlorinated pesticides	10 min	0.4-1.2 ng g^{-1}	Chloroform, 35 μl	Fish	GC-ECD	[38]
UAE) coupled SBME	Chlorobenzenes	30 min	0.7-27.3 ng g^{-1}	Water, 10 ml	Soil	GC-MS	[39]
b) Ultrasonic-Assisted Liquid-Phase Microextraction (UA-LPME)							
UA-DLLME-SFO	Curcumin	-	1.2 ng ml^{-1}	1-Dodecanol, 50 μl	Human Serum	HPLC-UV	[40]
UA-DLLME	Imidacloprid	10 min	0.045 mg kg^{-1}	Tetrachloroethane, 30 μl	Tomato	HPLC	[41]
UA-LPME	Nitric oxide	2.5 min	2.5×10^{-13} M	CCl_4, 20 μl	PC12 cells	HPLC	[43]
UA-DLLME	Phthalate esters	2 min	1.0-1.2 mg l^{-1}	CCl_4, 20 μl	Bottled water	GC-FID	[44]
UA-DLLME	Pyrethroids	2 min	0.11-0.3 μl^{-1}	CCl_4, 20 μl	River water	HPLC	[45]
UA-IL-DLLME	Chromium (VI)	1 min	0.07 ng ml^{-1}	[Hmim][PF6], 50 μl	Water samples	ET-AAS	[46]
UA-R-IL-DLLME	ursolic acid	15 min	-	[Hmim][PF6], 100 μl	Force loquat capsule	RP-LC-UV	[47]

Table 1. Continued

UA-IL-DLLME	Biogenic amines	4 min	0.25-50 ng ml^{-1}	[C4MIM][PF6], 30 µl	Beer	HPLC-FD	[48]
UA-DLLME	Essential oil	13 min	0.2-29 ng ml^{-1}	Chlorobenzene, 100 µl	Oliveria decumbens Vent	GC-MS	[49]
UA-IL-DLLME	Copper, Nickel and Lead	10 min	0.17, 0.49, 0.95 µg ml^{-1}	$[C_4MIM][PF_6]$, 150 µl	Food samples	FAAS	[26]
USAEME	Propoxur	25 min	1 ng ml^{-1}	CCl_4, 40 µl	Environmental and beverage samples	HPLC-VWD	[50]
US-ILME	Aluminum	11 min	0.66 µg l^{-1}	$[Hpy][PF_6]$, 100 µl	Drinking water, blood and urine	FAAS	[51]
USAE-SFODME	Gold	13 min	0.45 ng ml^{-1}	1-Undecanol, 40 µl	Water and pharmaceutical samples	FAAS	[54]
c) Ultrasonic Nebulization Extraction Headspace Single-Drop Microextraction (UNE-HS-SDME)							
UNE–HS-SDME	Essential oil	20 min	14.8, 6.67, 10.1 pL l^{-1}	Water, 3 ml	Cuminum cyminum L	GC-MS	[56]
UNE	Anthraquinones	30 min	-	Ethanol 80%, 15 ml	Rheum palmatum L.	MEKC	[57]
UNE	Chemicals	10 min	1 ng ml^{-1}	Methanol/water (1/1), 4 ml	Tablets and biological tissues	LPPI	[58]
UNE-HS-IL-SDME	Essential oil	13 min	-	Water, 5 ml	Forsythia suspensa	GC-FID	[59]
UNE-HS-SDME	Volatile compounds	15 min	-	Water, 3 ml	Zanthoxylum bungeanum	GC-MS	[60]
UNE-HS-HFME	Pesticides	35 min	12.4-22.2 mg kg^{-1}	NaCl solution (10%)	Panax ginseng C.A. Mey	HPLC	[61]

COOLING-ASSISTED SOLID-PHASE MICROEXTRACTION (CA-SPME)

Cooling-Assisted Solid-phase Microextection (CA-SPME) by Liquid CO_2

In 1995, internally-cooled solid-phase microextraction (IC-SPME) technique was introduced to enhance the efficiency of SPME [8]. The IC-SPME device was successfully evaluated for the quantitative extraction of benzene, toluene, ethylbenzene, and xylene (BTEX) in clay soil samples. It used a Hamilton 1710RN gastight syringe barrel as the SPME device with discarding the plunger and needle and replacing by a 17-gauge needle. A silica capillary tube was used as fiber and a piece of polydimethylsiloxane (PDMS) liquid polymer tubing as fiber's coating. Other type of coatings such as polyacrylate (PA) and divinylbenzene (DVB) did not have this type of tubing and could not be coated on this large bore tubing. Therefore, this type of SPME device was bound to PDMS, as the only possible sorbent. A silica capillary was used to deliver liquid carbon dioxide into the plunger to cool the fiber. This tube was fragile and hard to use. Additionally, it was bound to a predetermined and non-adjustable flow rate induced by its internal diameter; so the flow rate of coolant liquid CO_2 was out of control. The system was difficult to automate and limited to 250 °C as maximum allowed temperature due to leakage probability. In general, using IC-SPME device was tedious, though, it was the starting point for improving the microextraction methods using cooled extraction phases.

This research remained inactive up to 2006 until a modified version of the previous design, named cold-fiber headspace solid-phase microextraction (CF-HS-SPME) device [16,62], was introduced. In this new automated miniaturized design a piece of PDMS tubing was accommodated into an 18-gauge stainless steel needle, as the fiber's coating. This setup was robust and easy to use and automate [8]. The CF-HS-SPME design used a 33-gauge stainless steel tubing to deliver liquid carbon dioxide for cooling the fiber. Moreover, a handmade restrictor was made and used for adjustable and precise control of flow rate and, control of coating's temperature at smaller intervals. Unlike the previous system, using an adjusting tube prevented the fiber's coating to be stripped in contact with edges of a needle during movement through its inside and outside. In addition, there were no leaks in the system. The proposed CF-HS-SPME device was mounted on an autosampler arm and full-automatically used. This system was successfully applied for direct extraction of polycyclic aromatic hydrocarbons (PAHs) in sediment samples, with minimal manipulation.

The CF-HS-SPME setup was also coupled to GC-FID and GC-MS and applied for chemical screening of volatiles from tropical fruits [63]. It was coupled to a gas chromatography time-of-flight mass spectrometric detection (GC-TOF-MS) and applied to determine the flavor profile of fragrant rice samples [64]. The results showed that uncooked rice samples can be successfully analyzed even as dry kernels, without addition of water. It was also applied to determine chloroanisoles in cork samples [65]. In 2009, the CF-SPME device coupled to GC-FID was used to trap and analyze the nano-scale aerosols [66]. Furthermore, in 2009, the automated CF-SPME system was developed to study the desorption kinetics of PAHs from different laboratory-spiked sand samples and naturally contaminated sediments [67]. In another research, PDMS (as a proper photoreaction medium) was utilized as the sorbent in the CF-SPME system (as a convenient tool to perform UV exposure) and injected into GC after extraction, to monitor the photodegradation volatile products [68] (Fig. 3). Indeed, hexachlorobenzene (HCB), as a model volatile, was absorbed on the cooled fiber of the CF-SPME device and then exposed to UV irradiation. So, "in situ" photolysis took place on the PDMS coating. As the main significance of this research, the problems of analyte losses associated to volatilization, in the conventional room temperature photo-SPME studies, was eliminated by cooling the fiber to 0 °C.

More evaluation of CF-SPME was continued in 2011 by introducing a new optimization procedure for gaseous phase sampling of PAHs and phthalic acid esters (PEs) [69]. The CF-SPME was further evaluated by combination of direct (DI) and headspace (HS) modes for determination of PAHs and PEs in soil samples [70]. To increase the extraction of analytes with different volatilities, the direct extraction mode was changed to the headspace in an individual analysis and, simultaneously, extraction time and coating's temperature were manipulated. The results showed that in DI mode low volatile analytes were more extracted, while

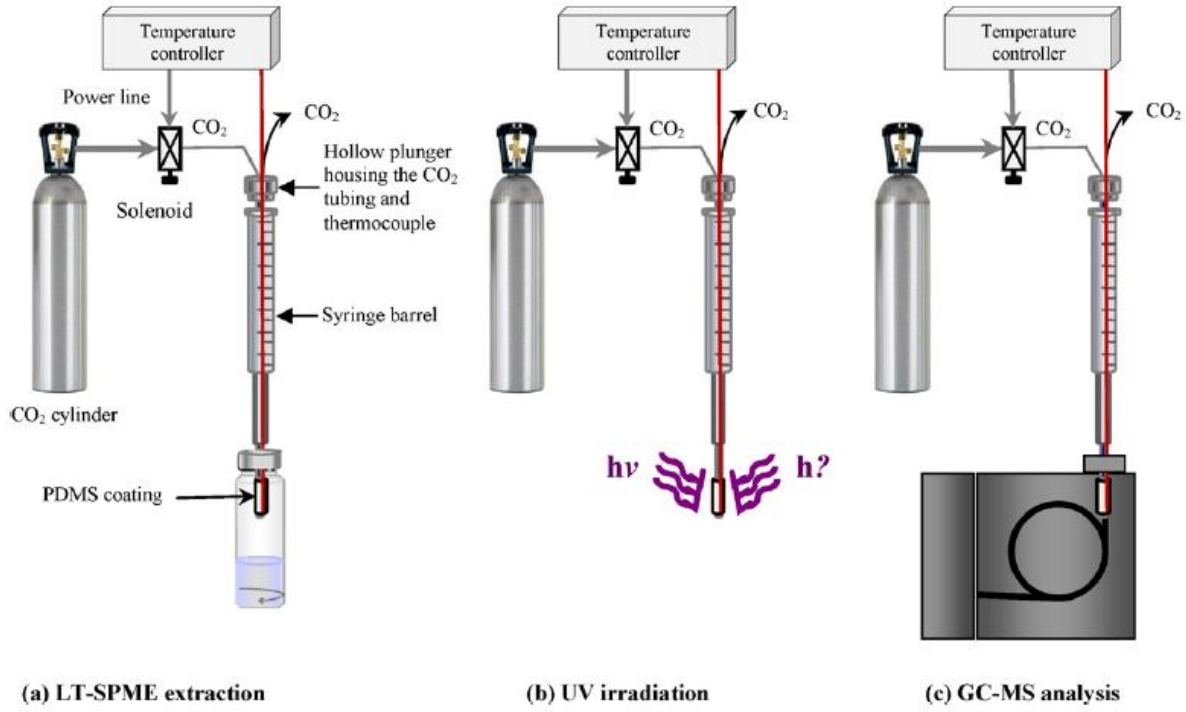

Fig. 3. The schematic of CF-SPME assisted photodegradation by UV-Irradiation setup a) sorption of analytes into the PDMS fiber of CF-SPME, b) UV irradiation absorbed analytes, and c) separation and identification of HCB and its photolysis products [68].

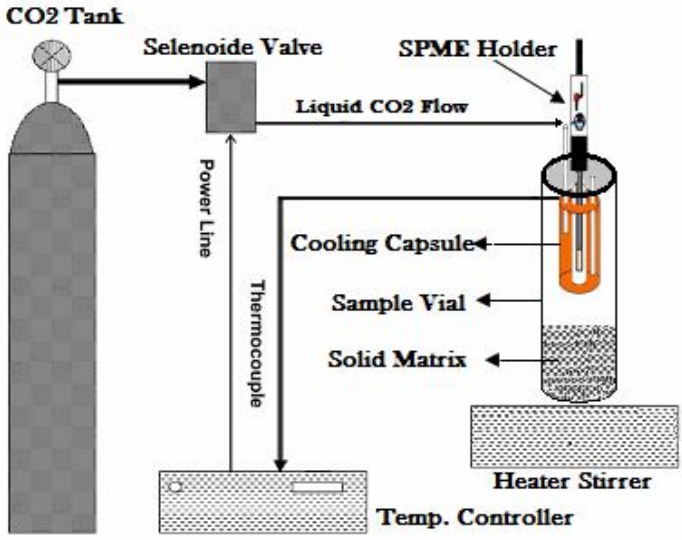

Fig. 4. Schematic representation of the CHA-HS-SPME device for direct determination of PAHs in polluted soil samples [74].

HS mode was appropriate for more volatile ones. Another report was published in 2012 by using the automated CF-SPME-GC-MS for the recovery and determination of compounds with varying volatility and polarity in different matrices [71]. A similar report was released in 2013 based on comparing two different coating's temperatures by CF-HS-SPME procedure to study the volatile profiles in six medicinal herbs [72]. The performance of the CF-HS-SPME setup for the exhaustive extraction of PAHs from solid matrices was theoretically and experimentally investigated to evaluate other aspects of the CF-SPME device [73].

As a new effort to amendment of CA-ME methods, a new cooling/heating-assisted headspace solid-phase microextraction (CHA-HS-SPME) setup was introduced in 2015, for direct extraction of PAHs from contaminated soils [74]. It was tried to design and develop a simple, low cost and effective cooling/heating-assisted SPME device, which compensate the limitations of the previously reported systems. The CHA-HS-SPME system used liquid CO_2 for efficient cooling like IC-SPME, while the cooling zone and the heating zone were somewhat separated (Fig. 4). This strategy let the fiber be effectively cooled without being seriously affected by the heat of the sample matrix. It was coupled to GC-FID and applied for the extraction and determination of PAHs in polluted soils, without any sample pretreatment step. The CHA-HS-SPME setup was able to be applied for cooling other types of sorbents like homemade fibers, needle trap devices (NTDs) and inside needle capillary adsorption trap (INCAT). Following the amendment of CHA-HS-SPME system, it was evaluated for cooling the extraction phase in LPME method. It was coupled to GC-FID through a hollow-fiber based LPME procedure (along with using low boiling point organic solvents) and utilized for direct extraction and determination of PAHs in contaminated soils [75]. The reported CHA-HS-SPME device was further modified and validated for cooling of the extraction phase (poured into a micro-cup) in headspace liquid-phase microextraction (HS-LPME) procedure, to increase the possibility of using volatile organic solvents without the use of hallow-fiber. This new setup was named cooling-assisted HS-LPME (CA-HS-LPME) and coupled with high-performance liquid chromatography (HPLC) and used to extract and determine safranal in Saffron samples [76].

Cooling-Assisted Solid-phase Microextection (CA-SPME) Based on Thermoelectric Cooler

Despite all benefits mentioned for CF-SPME, there are some limitations associated with this new device. It has several separate parts which make it complex and not feasible to apply in field studies. Moreover, its syringe construction is really tedious. Although, these drawbacks can be addressed by further modification of the system, there is still a need to develop a compact system with fewer parts, easier construction process, and practically applicable for proper field sampling. TEC, which has been used in miniaturized analytical instruments [77,78], could be a proper alternative cooling tool for CF-SPME. For instance, TEC has low cost, small size, low weight, no moving parts, and can precisely control the temperature. However, the most important requirement to achieve higher efficiencies is the ability to transfer cool directly to the extraction phase.

The first report on using TEC technology in the SPME sampling was developed by Haddadi *et al.* [79]. In this work, a new CF-SPME device was designed based on a copper rod coated with PDMS as the SPME fiber, and a three-stage TEC for cooling it. The proposed TEC-CF-SPME device was coupled to GC-FID and utilized for the quantitative analysis of off-flavors in rice samples. Another CF-TEC-SPME study was performed using poly(3,4-ethylenedioxythiophene) (PEDOT) and graphene oxide (GO) nanocomposite, electrochemically coated on gold wire as fiber, and a commercial TEC instrument [80]. The new SPME fiber was applied for the extraction of PAHs from aqueous samples in direct immersion (DI) and headspace (HS) modes. Regardless of sample types, the obtained linear dynamic ranges (LDRs) and limit of detections (LODs) for PAHs were not comparable with those reported by CF-HS-SPME using internally cooled fiber [16,62]. Despite advantages of TEC-CF-SPME setup, it was the lack of a proper efficiency when high temperature gaps were applied between sample matrix and fiber's coating. This fact is revealed from the extraction temperature profile, which is similar to the temperature profile of the conventional SPME [81]. The lower recovery of more volatile PAHs is another proof for inefficient cooling of the fiber by the TEC system. The main disadvantage of the TEC-CF-SPME device is indirect transmission of cooling onto the fiber. The heat of the sample matrix is directly transmitted onto HS and

consequently onto the fiber's coating, while cooling the fiber by the TEC occurs through fiber's core. This indirect cooling process is not able to cool the fiber properly as it is heated by HS. Therefore, when the temperature is preset, the temperature felt by the coating is considerably high. This fact has been clearly described by calibrating the first version of the TEC-CF-SPME device [79], at which the temperature of the fiber was plotted versus the temperature of the cold side of TEC for a range of temperatures. This calibration plot showed that the superficial maximum temperature gaps which can be created between fiber and HS are not so significant (*i.e.*, 65 °C in reference [80] and 70 °C in reference [79]), whereas IC-SPME can create temperature gaps over 200 °C [8,16,64,74].

The previously described TEC-CF-SPME device [80], with electrochemically reduced graphene oxide (R-GO) as fiber's coating, was used to extract tricyclic antidepressants (TCADs) from water samples [82]. Similar to the last cited report [80], the temperature profile of the proposed method with cooling is more similar to that of CA-SPME, based on thermoelectric cooler.

Cooling-Assisted Solid-phase Microextection (CA-SPME) Using Circulating Cooled Fluids

Ice, alcohol and cold water have also been used to cool the extraction phase in different CA-ME setups, in addition to liquid CO_2 and thermoelectric cooler. Achten and co-worker extracted methyl *tert*-butyl ether (MTBE) from surface water samples by a CF-SPME setup, and hyphenated to GC-MS [83]. A cooling cylinder filled with ice was placed around a commercial SPME fiber holder to cool it to 5 °C and sample's temperature varied over 5-30 °C during the extraction. A disadvantage of this method was rapid contamination of the ion source, due to the entrance of water vapor and low-volatility organic materials into the MS system. Considering these drawbacks, a new CF-HS-SPME-GC-MS method was developed for the extraction and determination of MTBE in water samples [84]. A SPME manual fiber holder, with a polydimethylsiloxane/carboxen (PDMS/CAR) coating, was cooled to 0 °C by a commercial cryostat, while sample temperature was kept constant at 35 °C during the extraction. Using the proposed CF-SPME procedure in HS mode, MTBE was extracted almost four times more than DI mode. Moreover, the pollution of the ion source by water and less volatile VOCs present in aqueous sample solution could be avoided. It should be noted that this setup [83,84] cools down the fiber through the cooling of SPME-holder body that is not efficient to create suitable temperature gap between the fiber and the sample matrix. Thus, it can be easily predicted that at elevated temperatures, the temperatures of the fiber and the same matrix will be almost the same.

In another research, a new HS-SPME device was fabricated and coupled to an ion-trap tandem mass spectrometer (IT-MS/MS) and used for the determination of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in contaminated soils [85]. This system was equipped with an alcohol-circulating cooling part around the upper part of the extraction vial, a heating water-bath, and an ultrasonic agitation device. A commercial manual SPME fiber holder and a PDMS fiber were used for the extraction of all analytes. To enhance both steps of releasing the analytes from native matrix and trapping them, the fiber coating was cooled by chilled alcohol and simultaneously, the sample was heated and agitated ultrasonically. The proposed CF-HS-SPME method was fast, efficient, and economical for screening the PCDDs and PCDFs compounds in soil samples. However, similar to the two recently described setups [83,84], cooling is not directly transmitted to fiber's coating. Headspace of the sample vial is cooled from the outside which could not be a reliable method to cool down the fiber. So, the temperature of the fiber coating does not exactly match with that of the chilling system, due to being affected by the heated sample and headspace. Thus, the temperature gap between the sample matrix and the fiber's coating cannot be significantly high. The maximum temperature applied to the sample matrix was 85 °C and the minimum temperature of the chilling system (not the exact temperature of the fiber's coating) was 4 °C, while the corresponding values obtained in previous reports were 250 °C and -20 °C, respectively [16].

The further development of the CA-SPME method [83,84] was continued by a report in which the effect of freezing out of aqueous samples, on enhancement of sensitivity and precision, was studied [86]. In this study, temperatures of the fiber and aqueous sample solution were

kept at -20 °C. Then, the result was compared with those obtained in a situation where the temperatures of sample solution and fiber were 35 and 5 °C, respectively. Several analytes with different hydrophobicity and partition coefficients were extracted from the aqueous samples using a commercial PDMS fiber followed by GC-MS analysis. Another setup named "circulating cooling solid-phase microextraction (CC-SPME)" was developed in 2006 [87]. It was coupled to gas chromatography-electron capture detector (GC-ECD) and applied to determine organochlorine pesticides (OCPs) in aqueous samples. It used an iced water circulating system along with an Environmental Protection Agency (EPA) standard sample vial. After adsorption of analytes, ACF was removed by the SPME fiber holder and injected into a GC-ECD. A modified version of the CC-SPME setup, named cold activated carbon fiber SPME (CACF-SPME), was introduced in 2007 and coupled to GC-ECD to analyze OCPs in solid samples [88]. The results showed that the matrix had a significant effect on the sensitivity of CACF-SPME procedure due to different characteristics of the soil samples. The temperature profile of the CACF-SPME system had an optimum point, just like what happened to conventional SPME [81] and TEC-CF-SPME [82,83]. Thus, it can be concluded that this setup cannot create large temperature gaps between the sample matrix and the fiber's coating.

A different cooling-assisted setup coupled to HS-SPME was developed in 2007 and named cloud vapor zone HS-SPME (CVZ-HS-SPME) [89]. It used a conventional distillation apparatus and a bi-temperature-controlled (BTC) system for simultaneous heating the sample flask and cooling vapor inside a condenser, resulting in the formation of a dense cloud of analyte-solvent vapor for HS-SPME sampling (Fig. 5). A commercial SPME fiber holder was located on the end of the condenser using a proper septum. This combination was similar to the hydrodistillation-headspace solvent microextraction (HD-HS-SME) setups, which were previously applied for the chemical screening of the essential oil of medicinal plants [90]. The CVZ-HS-SPME system was coupled to GC-ECD and applied for the analysis of aqueous chlorothalonil samples. The peak area rises with increase in the sample temperature up to 130 °C and then remains constant up to 150 °C. The phenomenon is unlike the conventional SPME [81] and TEC-CF-SPME [79,80,82], and somewhat similar to IC-SPME [8,62]. This proves that the cooling process here is more effective and relatively unaffected by the heating of the sample matrix, due to separate locations of the sample and the vapor phase. Therefore, in addition to the direct cooling of the extraction phase, another effective strategy to enhance the efficiency of the cooling-assisted systems is separating the heating and cooling zones.

Following the studies conducted to improve the SPME characteristics, another setup was introduced in 2011 [91]. In this research, a new direct immersion cold-fiber SPME (DI-CF-SPME) method was developed and coupled to GC-MS for the determination of PAHs in ambient air particulates. A copper tube was employed to transfer liquid N_2 from a Dewer flask to the CF-DI-SPME device. One end of the tube was inserted into the N_2 flask, and the other end was rounded the needle of a manual SPME fiber holder, as a spiral. Another copper tube was used for controlling the nitrogen pressure in the Dewer flask as a regulating valve. The needle and fiber were cooled meanwhile passing and subsequent evaporating the liquid nitrogen through the spiral. The temperature profile of the DI-CF-SPME method is in accordance with conventional SPME.

The previously described CF-SPME device [91] was coupled to a standard gas generator chamber [92] and GC-MS and used to determine naphthalene in ambient air using commercial PDMS fiber [93]. Moreover, it was coupled to GC-MS and carried out for the determination of PAHs in spring water [94]. Analytical specifications of the studied CA-SPME techniques are summarized in Table 2.

Thin Film Microextraction (TFME) by Cooled Membrane

For further evaluation of TEC in different extraction methods, a thin film microextraction (TFME) method with a cooled membrane was introduced [95,96]. In this way, the advantages of cold fiber SPME (CF-SPME) and TFME were merged in a new setup, named cooled membrane device (CMD). The TFME-CMD setup was coupled to GC-MS and used for sampling and quantification of several fragrance analytes with different volatilities.

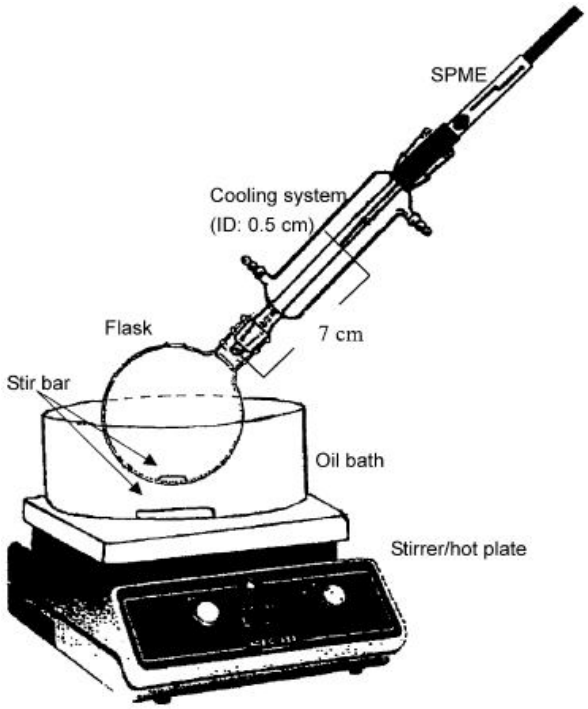

Fig. 5. Representation of the proposed CVZ-HS-SPME setup [89].

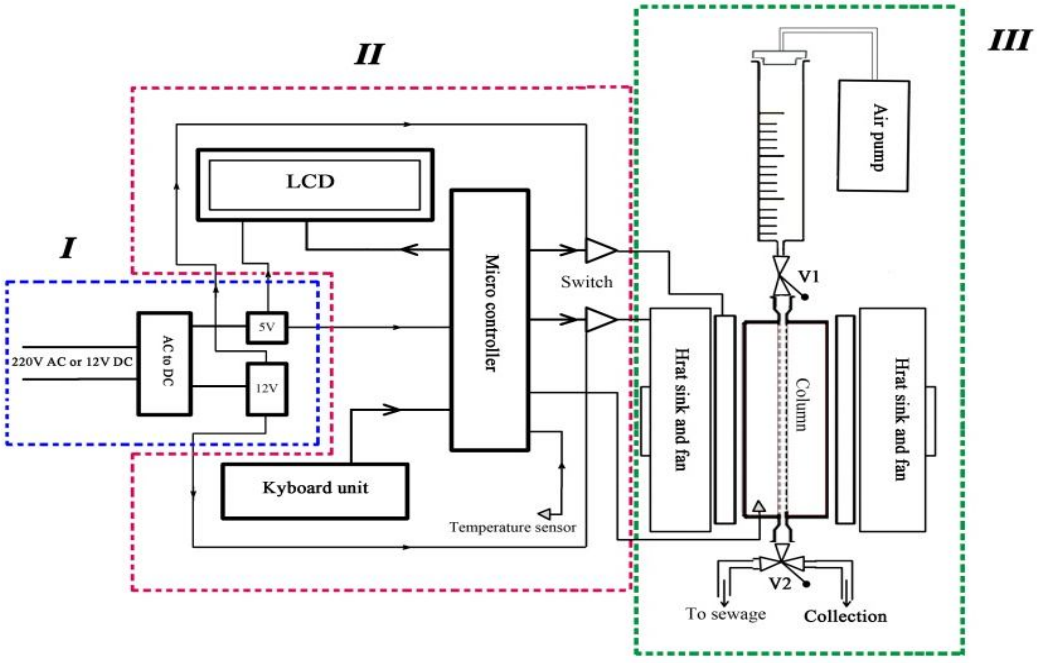

Fig. 6. Diagram of the main parts of the CCT-DLLME device [105].

Table 2. A Summary Review of the CA-SPME Techniques, which have been Applied for the Extraction of Organic Compounds in Various Matrices

Technique	Analyte	Extraction time (min)	Sample matrix temperature (°C)	Fiber temperature (°C)	Matrix	Detection system	Ref.
a) CA-SPME using liquid CO_2							
IC-SPME	BTEX	2-5	110 80	-17 35	Sand Water	GC-MS	[8]
Auto-CF-HS-SPME	PAHs	180	200	5	Sediment	GC-FID	[16]
Auto-CF-HS-SPME	BETX and PAHs	3	100	10	Air	GC-FID	[62]
CF-HS-SPME	Volatile compounds	30	80	0	Fruit	GC-MS	[63]
Auto-CF-HS-SPME	Flavor compounds	30	90	5	Rice	GC-TOF-MS	[64]
Auto-CF-HS-SPME	Chloroanisoles	10	130	10	Cork	GC-MS	[65]
CF-HS-SPME	Nano-scale aerosols	05-5	25	-75	Air	GC-FID	[66]
Auto-CF-HS-SPME	PAHs	5-60	150	25	Spiked-sand	GC-FID	[67]
CF-SPME	UV-volatile photoproducts	45	50 ± 8	0	HCB in water	GC-MS	[68]
CF-SPME	PEs, PAHs	23	140	10	-	GC-FID	[69]
DI/HS-CF-SPME	PAHs and PEs	50 DI, 30 HS	90	30	Spiked soil	GC-MS	[70]
Auto-CF-SPME	14 Analytes with different volatilities and polarities	20	80	30	Water, Spiked silica gel	GC-MS	[71]
CF-HS-SPME	Volatile compounds	7.5 SPME, 7.5 CF-SPME	60	5	Medicinal herbs	GC-MS	[72]
CF-HS-SPME	PAHs	30	200	30	Spiked sand, CRM soil	GC-FID	[73]

Table 2. Continued

b) CA-SPME by TEC							
TEC-CF-SPME	Hexanal, Nonanal and Undecanal	30 5	70 110	≈ 20 ≈ 30	Rice	GC-FID	[79]
TEC-CF-SPME	PAHs	20	80	Not reported	Sea water	GC-FID	[80]
DI/HS-TEC-CF-SPME	TCADs	60 90	50 DI 70 HS	Not reported Not reported	Water	GC-FID	[82]
c) CA-SPME using circulating cooled fluids							
CF-SPME (cooling of fiber-holder by ice)	MTBE	60	18-19	5	Surface water	GC-MS	[83]
CF-SPME (Cooling of fiber-holder using commercial cryostat)	MTBE	30	35	0	Surface water	GC-MS	[84]
CF-SPME (cooling of HS of sample by chilled alcohol	PCDDs and PCDFs	60	85	4	Spiked soil	GC-MS/MS	[85]
CF-SPME (simultaneous freezing-out of aqueous and fiber)	VOCs	30	-20 and 35	-20 and 5	Aqueous sample	GC-MS	[86]
CC-SPME (cooling of sample HS in EPA vial by iced water circulating)	OCPs	25	80	Not reported	Water	GC-ECD	[90]
CACF-SPME(cooling of sample HS in EPA vial by iced water circulating)	OCPs	60	60	Not reported	Soil	GC-ECD	[88]
CVZ-HS-SPME (cooling of HS vapor in a condenser)	Chlorothalonil	15	130	5	Aqueous sample	GC-ECD	[89]
DI-CF-SPME (cooling of fiber-holder needle with liquid N_2)	PAHs	60	70	Not reported	Air particulate	GC-MS	[91]
CF-SPME (cooling of fiber-holder needle with liquid N_2)	Naphthalene	15	40	Not reported	Ambient air	GC-MS	[93]
CF-SPME (cooling of fiber-holder needle with liquid N_2)	PAHs	60	60	Not reported	Spring water	GC-MS	[94]

COOLING-ASSISTED LIQUID-PHASE MICROEXTRACTION (CA-LPME)

Cooling-Assisted Liquid-phase Microextraction (CA-LPME) Using Thermoelectric Cooler

The extracting solvent, in different modes of HS-LPME, should have a low vapor pressure and high boiling point, to reduce the probability of vaporizing the drop. Moreover, to select a proper solvent other physical and chemical characteristics such as purity, viscosity, selectivity, solubility in water, extraction efficiency, incidence of drop loss and low toxicity should be also considered. While using GC or even HPLC system, another limitation associated with the solvent peak may interfere with the eluting analytes. So, HS-LPME is restricted to a limited number of solvents with high boiling points such as 1-octanol, cyclohexane, n-decane, n-hexadecane, and ionic liquids (ILs) [97]. When HS-LPME is coupled to GC, the solvents with boiling points higher than 100 °C will produce long and broad peaks and may interfere with target analytes. Different approaches were proposed to solve this problem [98]. However, lowering the temperature of the extracting solvent (*i.e.* in CA-LPME) is the most effective thought to prevent the vaporization during HS extractions [99-102].

The first report on using TEC for cooling the extraction solvent in HS-LPME method was published by Chen *et al.* for the extraction of chlorobenzenes (CBs) using volatile organic solvents [103]. The organic solvent suspended into a cylindrical cavity of a polytetrafluoroethylene (PTFE) vial cap, was exposed to the HS of the extraction vial, containing the aqueous sample. A proper TEC device was constructed and used for cooling the organic solvent in PTFE vial cap. This reformation enabled HS-LPME to use volatile solvents such as acetone and dichloromethane and also use larger volumes of them. Another similar research, named gas-purged headspace liquid phase microextraction (GP-HS-LPME), was conducted to perform rapid automatic extraction of the trace analytes [104]. A semiconductor condenser and a heater were embedded in the proposed system for cooling the extractant and heating the sample. The proposed GP-HS-LPME device, coupled to GC-MS, was applied to extract and quantify volatile and semi-volatile PAHs from spiked samples. Then the results were compared with the conventional HS-LPME-GC-MS strategy.

Following the efforts to develop liquid microextraction methods based on cooled extractant, a new article was released in 2012 [105]. A commercial TEC system was fixed in a proper setup and used for cooling the extraction phase in a DLLME method. So, a controlled cold-column trapping (CCT) system was developed and coupled to DLLME for quantification curcumin in aqueous samples using HPLC-UV (Fig. 6). This portable CCT-DLLME device has eliminated the centrifugation step in DLLME procedure. In this setup, the dispersed organic extraction solvent was collected on the glass beads packed in a proper column and then solidified and trapped using the CCT system. The separated extracting phase was then eluted in an elevated temperature, using another organic solvent. However, unlike the previously described systems, CCT did not create high temperature gaps and was used only to solidify and melt 1-dodecanol between 10 and 30 °C, respectively. The CCT device was also coupled to a CPE method and used for the extraction of curcumin in human urine [106].

Cooling-Assisted Liquid-phase Microextraction (CA-LPME) Reinforced by Circulating Cooled Fluids

In continuing research on the CF-SPME using liquid CO2 [8,16,62], other techniques were developed to cool the extraction phase in different modes of LPME. Accordingly, a new headspace solvent microextraction (HS-SME), based on a water circulator, to control the temperature of the organic drop, was introduced by the name of temperature-controlled organic drop headspace solvent microextraction (TC-OD-HS-SME) [107]. Two separate recirculation systems, connected to two corresponding water baths, were used for adjusting the temperature of the sample solution and the organic microdroplet. To achieve the equilibrium temperature, the internal part of the re-circulating compartment was made of stainless steel and closely fitted to the outer wall of the needle. To evaluate the reliability of the proposed HS-SME-GC-FID strategy, it was employed to extract and quantify 2-butoxyethanol from paint samples. This system could control the temperature of microdroplet over the range of 2.5-25 ℃; however, cooling the system to the temperatures much lower than zero was not practically

feasible. Additionally, the direct temperature control continues just to the time when the organic solvent is left into the microsyringe. Afterwards, when the microdroplet is suspended into the HS of the sample solution, the temperature control is terminated. Another report based on CA-LPME was released by Huang *et al.* [100]. In this study, a cooling-assisted dynamic hollow-fiber-supported headspace liquid phase microextraction (DHF-HS-LPME) method was developed. A hollow fiber (HF) was soaked with an organic solvent and employed as an extraction medium. The HF was fitted to a syringe needle and exposed to the headspace of the sample solution. To enhance the mass transfer of analytes, the extracting solvent was moved up and down within HF using a programmable syringe pump. Large surface area of HF not only can improve the extraction efficiency, but can also increase the risk of solvent loss due to evaporation, because the recirculating compartment has been fitted to the outer wall of the syringe barrel, similar to the previously described study [107]. The proposed DHF-HS-LPME method was coupled to GC-MS and successfully applied to extract and determine OCPs in river water samples.

Shi and coworkers introduced a microwave-assisted controlled-temperature headspace LPME (MA-HS-LPME) method for analysis of chlorophenols in landfill leachate samples [99]. A household microwave was used to heat the sample and accelerate the evaporation of the analytes into the HS. An external cooling system was used to control the temperature of the HS sampling.

For analysis of semi-volatile VOCs by HS-LPME, the main problem concerns to low boiling point of the organic solvents, which causes them to evaporate rapidly during the extraction process. To overcome these limitations, the hollow-fiber-supported HS-LPME (HF-HS-LPME) [108,109] and, consequently, the dynamic hollow-fiber-supported HS-LPME (DHF-HS-LPME) were introduced [110]. In the HF-HS-LPME approach, the hollow fiber was filled with extracting solvent, hanging from the tip of a microsyringe needle and exposed to the HS of sample solution. The solvent was moved to-and-fro into the HF using a microsyringe or a syringe pump [100]. The DHF-HS-LPME method has still some limitations. For example, gradual withdrawal of the organic solvent from the straight HF (usually 1.5 cm) during the extraction process causes to enter the air bubbles into it. These bubbles make the conditions difficult for the pump to withdraw exact portions of the solvent after the extraction. Thus, it is not suitable to use longer fibers or higher volumes of the extracting solvent (for more extraction contact interface). Moreover, heating the sample solution, for more efficient releasing the analytes, will exceed the evaporation of a limited volume of the extracting solvent. To address the above-mentioned drawbacks, a new setup called dynamic headspace time-extended helix liquid-phase microextraction (DHS-TEH-LPME) [102] was introduced, in which a 4.5 cm piece of HF filled with 13 µl of the extracting solvent and bent around the syringe needle, as a helix shape. The end of the fiber was affixed to the bottom of syringe barrel using a pin. The excess portion of the solvent exited from the fiber and formed a large droplet, suspended within the helix of the fiber. Such a combination prevents the interference of air bubbles and provides the organic microdroplet remaining unbroken. A larger volume of microdroplet and longer HF length caused wider contact interface and, consequently, efficient extraction at a shorter time. The proposed DHS-TEH-LPME setup was equipped with a cold-water recirculation compartment to lower temperature of the extracting microdroplet.

The previously described MA-HS-LPME system [99] was used to extract hexachlorocyclohexanes (HCHs) in aqueous matrices, followed by GC-ECD separation and determination [111]. A household microwave was utilized for heating the sample and enhancing the evaporation of HCHs into the HS, and an external-cooling compartment was used to control the temperature of the HF (in the sampling zone). Due to the sudden cooling of the vapor, the external cooling system provides a dense cloud of analyte-water vapor in the HS. This new setup was named as microwave-assisted headspace controlled-temperature LPME (MA-HS-CT-LPME).

The MA-HS-CT-LPME system, firstly introduced by Huang *et al.* (2007) [89] and developed by Shi *et al.* [99] and Tsai [111], was used by Ponnusamy *et al.* in different modes of LPME [112]. In this new research, irradiation of a household microwave was used for enhancing the efficiency of SDME of chlorophenols from aqueous samples. To this end, an organic microdrop was suspended at the bottom of a micropipette tip, affixed to a HPLC microsyringe needle. A

water recirculating cooling system was utilized to control the temperature of the sampling zone around the SDME microdroplet. The recirculating system utilized cooling water from a refrigerator machine to set the vaporized analytes at a constant temperature (1 °C). Therefore, the vapor quickly formed a dense cloud of analyte-water vapor near the microdrop and enhanced the trapping of analytes by the SDME solvent. The developed MA-HS-CT-SDME setup was then coupled to HPLC-UV to extract and determine the chlorophenols in river water. It should be noted that this multipart setup is complicated and labor-intensive. More specially, the household microwave is dangerous and may cause explosion or splashing out the samples in high microwave powers.

Gas-Purge Microsyringe Extraction (GP-MSE) with Cooling System

The gas flow headspace LPME (GF-HS-LPME) procedure was introduced by Yang *et al.* [113], to improve the efficiency of HS-LPME. In comparison with HS-LPME, it is faster, more economical and more efficient for volatiles due to increasing the analyte molecules in the gas phase. Despite the foregoing advantages, it has some limitations in its routine applications, such as low recovery for low-volatiles, operational difficulties due to easy driving out of the microdroplet and incomplete quantitative extraction. To overcome these drawbacks, the first effort resulted in a novel gas purge microextraction setup, which was named gas purge microsyringe extraction (GP-MSE) system [114]. A 100-µl microsyringe barrel was used as the "holder" and "protector" of the extracting organic solvent and a narrow stainless steel tube was fitted to the bottom of the microsyringe barrel to avoid running off the solvent. Thus, microdroplet stability was significantly improved using the microsyringe barrel and the cooling process. This approach increased the contacting surface area of the organic extracting microdroplet and led to quantitative recoveries of both volatile and semi-volatile analytes within a short extraction time. The proposed cooling-assisted GP-MSE device was coupled to GC-MS and used to determine PAHs, OCPs and alkyl phenols (APs) in plant and solid samples. This system was further amended and employed to analyze xylene, PAHs, OCPs, polychlorinated biphenyls (PCBs), and APs as the target analytes, with different volatilities [115].

Despite advantages of the GP-MSE setup, it is not suitable for direct analysis of analytes in water-based samples. Therefore, Yang *et al.* introduced a water-based GP-MSE setup, taking into account the compatibility of GP-MSE with LC and characteristics of the target compounds [116]. To this end, the GP-MSE system was partially modified which resulted in an environment-friendly solvent-free sample preparation technique. It can directly extract the target analytes from the wet samples without any drying process. The new water-based GP-MSE setup was coupled to HPLC-UV and used to extract and determine APs in seafood samples.

MISCELLANEOUS APPLICATIONS OF COOLING-ASSITING IN ANALYSIS

Apart from the investigations which take into account the cooling systems to trap and preconcentrate volatile compounds for analytical measurements, there are some cases in which other chemical and analytical purposes are considered. As miscellaneous applications of the cooling systems in analytical chemistry, TECs have been used in microfluidic devices (MFDs) in several studies [117]. The efficiency and reliability of the chemically and biologically oriented lab-on-a-chip studies depend on the ability to manipulate the contents of channels in MFDs. The microfluidic channels are of vital importance in MFDs, because they enable working with small sample volumes with accurate control of experimental conditions. The studies conducted on MFDs to date, have been able to formulate both streams and individual droplets of varying diameters [118]. The ability to manipulate small reaction vessels with high concentration of analyte in a small volume, and ease of controlling the chemical and physical conditions of these small vessels are among the advantages of droplets in MFDs. In one of such different applications of the cooling systems, TEC was used in cell signaling networks. A MFD was introduced which has enlisted a segmented gas-liquid flow to enhance mixing and use thermoelectric heaters and coolers to control temperature during cell stimulus and lysis [119]. There are also few reports in the literature on coupling of TEC to spectroscopic instruments, instead of separation techniques. In one of

these studies, a VOC sensor including a surface enhanced Raman spectroscopy (SERS) substrate, mounted on a TEC, was introduced [120]. The absorbing surface of SERS was coated with a thiol to prevent its oxidation and/or degradation. The TEC-SERS sensor was applied to determine chlorinated solvents, aromatic compounds, and MTBE. It was revealed that the response of TEC-SERS sensor to VOCs depended upon SERS surface temperature, nature of coating, VOC properties and gas flow rate. The results also indicated that TEC-SERS can be used as a field-deployable sensor. One of the most interesting applications of the cooling-assisted extraction systems was introduced using TEC for solid-phase dynamic extraction (SPDE) to produce an effective commercial extraction tool. Followed by sufficient development of TEC and its application in analytical extraction methods, it was merged into a SPDE as a new commercial analytical product. For proper introduction of SPDE, its history is of prime importance. The most effective arrangement to compensate the SPME drawbacks was proposed by Murphy *et al*., by introducing the "internally coated hollow needle" in which the coating was attached on the interior of a needle or capillary [121]. One year later, the INCAT device was introduced [122]. Another effort to compensate the SPME drawbacks resulted in a new technique called in-tube SPME, consisting of an open tubular fused-silica capillary column, whose interior is coated with a suitable coating [123]. Then, SPDE was developed by ChromTech Company (Idstein, Germany) as the first commercially available device. Afterwards, several studies were conducted with different analytes in various matrices, using SPDE [124,125]. In practice, higher volatile compounds are poorly trapped, because SPDE is usually applied at room temperature. Thus, ChromTech Company merged TEC into SPDE and introduced a new commercial analytical product, called SPDE Extraction Cooler. This arrangement was called SPDE Extraction Cooler, which can successfully extract high volatiles by intensive cooling of the needle. Thus, highly volatile analytes can be easily extracted using the SPDE Extraction Cooler. Despite all advantages of the SPDE Extraction Cooler, it cannot create significant temperature gaps between the sample matrix and the extraction phase.

CONCLUDING REMARKS AND FUTURE TRENDS

The results of the first part of this literature survey demonstrated that the ultrasound irradiation enables the DLLME process to be performed without a disperser solvent. It can be also useful for enhancing the efficiency of conventional DLLME (when a dispersing solvent is also used) and the efficiency of ionic liquid-based DLLME as well. Ultrasonication encourages emulsification and dispersion of IL into the sample solution and improves the formation of the cloudy state. It was also noticeably indicated that the use of ultrasonic irradiation in different LPME methods continues to expand and consequently interesting and challenging applications can be anticipated in the near future.

As the results of the second part, different aspects of the CA-ME methods such as fabrication methods, applications, and analytical figures of merits were evaluated and compared. The results of this study point out several aspects for further development and modification of cooling assisted methods including (1) feasibility of handling various types of extraction phases, (2) possibility of direct cooling of the extraction phase, (3) feasibility of creating distance between heating and cooling zones, (4) being portable and applicable in field studies, and (5) using low cost and compact cooling systems such as TEC. In this case, heating the sample even to high temperatures cannot prevent cooling the extraction phase. Thus, creating large temperature gaps between the sample and headspace will be possible, and direct analysis of complicated solid samples with minimal manipulation can be performed.

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Acronym	Full Term
ACF	Activated Carbon Fiber
APs	Alkyl Phenols
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
CA-LPME	Cooling-Assisted Liquid-Phase

	Microextraction
CA-ME	Cooling-Assisted Microextraction
CA-SPME	Cooling-Assisted Solid-Phase Microextraction
CBs	Chlorobenzenes
CC-SPME	Circulating Cooling Solid-Phase Microextraction
CCT	Cold-Column Trapping
CF-SPME	Cold-Fiber Solid-Phase Microextraction
CHA-HS-SPME	Cooling/Heating-Assisted Headspace SPME
CMD	Cooled Membrane Device
CPE	Cloud Point Extraction
CVZ	Cloud Vapor Zone
DHF-HS-LPME	Dynamic Hollow-Fiber Supported Headspace Liquid-Phase Microextraction
DI	Direct Immersion
DLLME	Dispersive Liquid-Liquid Microextraction
DTD	Direct Thermal Desorption
DVB	Divinylbenzene
ECD	Electron Capture Detector
EPA	Environmental Protection Agency
GC-FID	Gas Chromatography-Flame Ionization Detection
GC-MS	Gas Chromatography-Mass Spectrometry
GF-HS-LPME	Gas Flow Headspace Liquid-Phase Microextraction
GO	Graphene Oxide
GP-MSE	Gas-Purge Microsyringe Extraction
HCHs	Hexachlorocyclohexanes
HD	Hydrodistillation
HF	Hollow Fiber
HLLE	Homogeneous Liquid-Liquid Extraction
HPLC	High-Performance Liquid Chromatography
HS	Headspace
IC-SPME	Internally-Cooled Fiber Solid-Phase Microextraction
INCAT	Inside-Needle Capillary Adsorption
LDR	Linear Dynamic Range
LLE	Liquid-Liquid Extraction
LOD	Limit of Detection
LPME	Liquid-Phase Microextraction
MA-HS-CT-LPME	Microwave-Assisted Headspace Controlled-Temperature Liquid-Phase Microextraction
MA-ME	Microwave-Assisted Microextraction
MFD	Microfluidic Devices
MEKC	Micellar Electrokinetic Capillary Chromatography
MS/MS	Tandem Mass Spectrometer
MSPD	Matrix Solid-Phase Dispersion
MTBE	Methyl *tert*-butyl Ether
NTD	Needle-Trap Device
OCPs	Organochlorine Pesticides
PA	Polyacrylate
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PDMS	Polydimethylsiloxane
PDMS/CAR	Polydimethylsiloxane/Carboxen
PTFE	Polytetrafluoroethylene
SA-ME	Solvent-Assisted Microextraction
SBME	Solvent Bar Microextraction
SDME	Single-Drop Microextraction
SERS	Surface Enhanced Raman Spectroscopy
SFODME	Solidified Floating Organic Drop Microextraction
SHS	Static Headspace Sampling
SME	Solvent Microextraction
SPDE	Solid-Phase Dynamic Extraction
SPE	Solid-Phase Extraction
SPME	Solid-Phase Microextraction
TEC	Thermoelectric Cooler
TEH	Time-Extended Helix
TFME	Thin Film Microextraction
TOF-MS	Time-of-Flight Mass Spectrometry
UAE	Ultrasonic-Assisted Extraction
UA-EME	Ultrasound-Assisted Emulsification Microextraction
UA-LPME	Ultrasonic-Assisted Liquid-Phase

	Microextraction
UA-ME	Ultrasonic-Assisted Microextraction
UA-SPME	Ultrasonic-Assisted Solid-Phase Microextraction
UNE	Ultrasonic Nebulization Extraction
US-MMSPD	Ultrasonic-Assisted Miniaturized Matrix Solid-Phase Dispersion
VOCs	Volatile Organic Compounds

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