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Recent Developments and Applications of Microextraction Techniques for the Analysis of Pesticide Residues in Fruits and Vegetables

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1. Introduction

Analysis of pesticide residues and other contaminants in fruit and vegetable samples is becoming increasingly important due to the health hazards caused by their accumulation in human tissue. The body requires some important nutrients which can be provided by the consumption of fruits and vegetables. The purpose of any analytical study is to obtain information about substances and analytes present in the sample. Analytical process involves several steps: sampling, sample preparation, separation, quantification and data analysis [1]. Sample preparation is a very important step and indeed the bottleneck of analytical methodologies, in the analysis of fruits and vegetables for the presence of pesticide residues in fruit and vegetable samples [2].

The first step in any instrumental analysis is sample preparation, which involves the isolation or extraction of the desired analytes from the sample matrix, since they are present at trace concentration (usually µg.kg or less). This helps in the elimination of any interferences and also reduces the volume of extracts, thereby concentrating the analytes [2]. The type, nature and composition of sample and the nature and concentration of analytes to be isolated or extracted determines the choice of separation and detection method to be used, and this also dictates the type of sample preparation to be employed [3, 4], since the efficiency of any analysis is determined by the sample preparation step. The current trend of microextraction techniques is aimed at a reliable and accurate analysis of contaminants from complex samples. It is focused on the reduction of sample and solvent volume, with the automation/coupling of the sampling step to the analytical instruments, while maintaining the high throughput performance, low cost operation and improvement of the sample preparation, such as extraction, concentration, isolation of analytes, and clean-up [5, 6].
The conventional solvent-based sample preparation methods: liquid-liquid extraction (LLE), solid phase extraction (SPE), accelerated solvent extraction (ASE), matrix solid phase dispersion (MSPD) [7-11], usually require various matrix pretreatment steps, which are tedious, time consuming, contains multistep techniques, require large volumes of sample and toxic solvents which impose environmental pollution and health hazards with high operation cost [5]. Therefore it is necessary to reduce the number of sample preparation steps in order to reduce the sources of error. Microextraction techniques are recently developed sample preparation methods which are vital as well as effective and efficient ways to save time, reduce solvent use and operation cost, and can efficiently measure the trace analytes embedded with high molecular mass compounds in complex sample matrices [12].

The microextraction techniques have been developed by different researchers, to corroborate the recent advances in the development of highly sensitive and efficient analytical instrumentation. Instrumental techniques like gas and liquid chromatography and capillary electrophoresis which are compatible with the microextraction technique, and coupled to different detectors (mass spectrometry, diode array detector, ultraviolet detector, etc), have been developed for qualitative and quantitative analysis of pesticide residues and other contaminants from foods. Prior sample preparation is necessary in order to extract, isolate and concentrate the analytes of interest from the complex fruits and vegetables matrices, which contain high molecular mass compounds. The low cost and ease of hyphenation of these microextraction techniques to analytical instruments helps to reduce errors, due to contamination and sample losses.

In this review, recent advances in different microextraction techniques used in the analysis of pesticide residues from fruit and vegetables are discussed, with a major focus on their methodologies, advantages, limitations and future trends.

2. Solid phase microextraction (SPME)

Solid phase microextraction, a solvent-free sample preparation technique, was developed by Pawliszyn and his co-workers in 1990 [13], and its applications has been examined, optimized and automated [14, 15]. It eliminates the need for solvents and combines sampling, isolation, concentration and enrichment in one step and offers the benefit of short sample preparation step, solvent-free extraction, small sample volumes and analyte concentration from solid, liquid or gaseous samples. It employs a chemically inert fused-silica optical fiber or metal alloys (Fiber SPME) coated on the outside with a thin film of sorbent [14] and a thin film internally coated fused silica capillary column (In-tube) [5, 16], as the extraction stationary phase, containing a polymeric organic compound. The fiber SPME has been widely used for the extraction of pesticide residues in fruits and vegetable samples, and will be discussed extensively in this review.

There are two major types of extraction modes used in the analysis of pesticides residues in fruit and vegetable samples. These are the headspace SPME (HS-SPME) and direct immersion SPME (DI-SPME). [5, 17-19]. The efficiency of each extraction mode is dependent
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on the sample matrix composition and the nature and volatility of the analytes. In the headspace sampling mode, the analyte is transported through a layer of gas before reaching the coating. The HS-SPME involves the exposure of the fiber to the vapour phase above a liquid or solid sample [5], where the analytes are extracted from the gas phase equilibrated with the sample matrix [20]. It could be effectively used for the extraction of analytes from complex liquid or solid samples [21]. This method helps to protect the coated fiber from the effects of any non-volatile high molecular weight compounds in the sample matrix, which binds irreversibly to the coating and often cause interference in the extraction process. In the DI-SPME, the coated fiber is completely inserted into the samples, where the transport of the analyte from the sample matrix into the extracting phase is achieved [22]. It is used for the extraction of gaseous or simple liquid samples.

The DI-SPME can also be applied for the extraction of analytes from complex samples, provided optimum dilution is achieved [18]. The HS-SPME is suitable for the extraction of volatile or semi-volatile and low- to medium-polar analytes, but the headspace volume should always be taken into consideration. The DI-SPME is used for the extraction of non-volatile analytes or analytes with low volatility and high-to-medium polar analytes [18, 21]. The advantage of HS-SPME over DI-SPME is the shorter equilibrium time, due to the higher diffusion coefficients in gaseous state, higher concentration of the analytes in the headspace prior to extraction and also allows for the variation of sample matrix properties without any effect on the fiber. Extraction mode is an important parameter which should be considered and optimized in the experimental design (described later) of SPME for a particular analyte under investigation.

There are two distinct steps in SPME; partitioning of the analytes between the extracting stationary phase and the sample matrix in DI-SPME mode and partitioning between fiber, headspace and sample matrix in the HS-SPME mode, followed by the desorption of concentrated extract [23], into analytical instruments, thermally when coupled to GC or with a mobile phase solvent when coupled to LC, and in the offline and online mode when combined with CE [12]. The technique is based on the partitioning of analyte and establishment of equilibrium between the analyte in the sample matrix and the stationary phase of the coated fused silica, which can either be liquid or solid particles suspended in a liquid polymer or a combination of both [14, 17, 24]. Recently, new SPME microextraction techniques have been developed, which make use of a microsyringe and is called in-needle SPME and with a pipette tip, known as in-tip SPME [12].

The experimental design of SPME for the analysis of pesticide residues from fruits and vegetables involves several steps and parameters which must be considered and optimized in order to achieve an efficient extraction. Parameters such as fiber type, extraction mode (described earlier), extraction and desorption time and temperature, separation and detection system, agitation method, ionic strength, sample pH, water and organic solvent content and method of calibration are considered and optimized based on the nature of analyte and constituent of sample matrix. Optimization of these parameters in the extraction of pesticide residues from food samples have also been reviewed in the literatures [5, 17, 22, 25, 26]. The first step in the development and optimization of an SPME method is the
selection of fiber coating, since the efficiency of SPME technique is dependent on the fiber coating/sample matrix distribution constant [18], because the extraction process involves the diffusion of analyte from sample matrix to the fiber/headspace, through the interface between the fiber/headspace and sample matrix.

The commercial fibers are coated with different polymeric materials (single or mixed), which extract by either absorption or adsorption. Due to their relative low recommended operating temperature (200 – 300 °C) of the commercially available fiber, the recent trend is focused on the development of new fibers using sol-gel technology, with high thermal stability (>320 °C) [27-37] and molecular imprinted polymers (MIPs) [38-42]. Ionic liquids and sol-gel prepared ionic liquid coated fibers have also been recently developed and have been used extensively for the SPME extraction of pesticide residues in water samples [43-46], but their use for the extraction of analytes from food samples is a potential research area to be explored in the future.

The PDMS is the most commonly used SPME fiber coating in fruit and vegetable analysis. Although, it is suitable for the extraction of non-polar pesticides, it has also been widely used for the extraction of more polar pesticides, after the extraction conditions have been optimized. [5]. The mixed coating: PDMS/divinylbenzene (DVB), DVB/PDMS/carboxen (CAR), carbowax (CW)/PDMS, CW/DVB and CW/template resin (TPR) extract by adsorption and possess complementary properties of each constituent polymeric coating.

The fiber SPME has been used successfully for the analysis of pesticide residues from fruit and vegetable samples. The 65 µm PA fiber was employed for the extraction of 54 multiclass pesticides from orange and peach in the DI mode [47]. The fiber coating was used for the extraction of phenyl urea pesticides from carrot, onion and potato in the DI mode [48], organophosphorus pesticides from orange, grape and lemon juice in the DI mode [49], triazole in strawberry in the DI mode [50], 14 multiclass pesticides from mango in the DI mode [51], while 80 µm PA fiber was used for the extraction of strobilurin fungicides from grape, ketchup, strawberry and tomato in the HS mode [52]. The 100 µm PDMS was used by Chai et al for the extraction of multiresidue organochlorine and organophosphorus pesticides from cabbage, tomato and guava in HS mode [53] and from strawberry, guava, pak-choi, tomato, star fruit and cucumber in HS mode [15, 54]. Organochlorine, organophosphorus and carbamate pesticides from tomato and cucumber in DI mode [55] has been employed. Organophosphorus pesticides was extracted from pear and apple in DI mode [56], strawberry, cherry and cherry juice in HS mode [57, 58], C. coronaium plant in DI mode [59] and 13 different vegetables in HS mode [60] using 100 µm PDMS. Multiclass pesticides were also extracted from tomato in the DI mode with 100 µm PDMS (Guillet [61].

A pre-extraction method, involving the use of matrix-assisted extraction followed by SPME extraction using the 100 µm PDMS was developed. The method was used for the extraction of organophosphorous pesticides from strawberry, tomato and pakchoi in the HS mode [62] and extraction of pyrethroid pesticides from strawberry in the DI mode [63]. The 100 µm PDMS gave better extraction efficiency, good linear range, lower detection limit and good recovery with relative standard deviation lower than 10%.
The most widely used mixed phase fiber for fruits and vegetables analysis is the 65 µm PDMS/DVB fiber. It was employed in the extraction of pyrethroid pesticides from tomato and strawberry [64], and 70 multiclass pesticides from cucumber, pepper and tomato [65]. The 60 µm PDMS/DVB fiber was employed for the extraction of 25 multiclass pesticides from tomato [61], carbamate pesticides from strawberry [66] and apple [67] and pyrethroid pesticides from cucumber and watermelon and 7 multiclass pesticides from tomato [68], the 65 µm PDMS/DVB coupled to multi-dimensional GC/MS was recently used for the analysis of multiclass pesticides in peach, orange and pineapple juices [69]. The less frequently used fibers in the extraction of pesticides from fruit and vegetable samples include the 65 µm CW/DVB, used for the extraction of carbamate pesticides from apple and grape juice [70], the 50 µm CW/TPR used for the extraction of postharvest fungicides from cherry, orange and peach [71], and multiclass pesticides in lettuce [72] and activated carbon/polyvinylchloride (AC/PVC) used for the extraction of organophosphorus pesticides from grape [73]. The extractions gave good repeatability and reproducibility with better efficiency than the single phase coated fibers.

3. Liquid phase microextraction (LPME) also called Solvent Microextraction (SME)

This is also a newly developed microextraction technique, which drastically reduces the quantity of solvent used for extraction [74]. It is rapid and less expensive, and is performed between a small amount of water-immiscible solvent called the acceptor phase, and an aqueous phase (donor phase) containing the analytes of interest [75]. The acceptor phase can either be immersed directly in the sample matrix or suspended above the sample for headspace extraction [12]. The volume of the receiving phase is in microliter (droplet of organic solvent). It is also known as liquid-liquid microextraction (LLME) and can be divided into three major categories and their difference is the way the extraction solvent comes in contact with the sample matrix.

1. Single Drop Microextraction (SDME)
2. Hollow Fiber Liquid Phase Microextraction (HF-LPME)
3. Dispersive Liquid Liquid Microextraction (DLLME)

The development of the methods for the analysis of pesticides by the LPME technique as in SPME, requires the optimization of the parameters related to the donor and acceptor phases. The first and the most important is the selection of an organic solvent which is of high purity, less volatile, high boiling point, so as to prevent solvent evaporation and ensure analyte concentration. The solvents should also be water immiscible for extraction of analytes from an aqueous sample. The SDME extraction like SPME is a non-exhaustive extraction method, thus an appropriate drop volume must be selected to prevent shrinking, and volumes are usually between 0.9 and 1.6 µL. Although, the use of a large volume of solvent drop yields better instrumental response and improve extraction efficiency, they are difficult to manipulate and could be easily dislodged from the syringe. Agitation increases the extraction efficiency, by decreasing the extraction time. It also leads to an increase in
aqueous mass transfer and exposes the analytes to the extraction solvent, and should be optimized to avoid the dislodgment of the solvent drop.

Salt addition enhances extraction efficiency by reducing the solubility of the analytes in the sample, especially for the moderately polar and low molecular weight analytes. The optimization of extraction temperature is important especially in the headspace mode, but a higher temperature may affect the stability of the microdrop, and for this reason most of the reported analyses have been carried out by DI-mode at room temperature. The sample and headspace volume should be maintained constantly at minimal level, since larger sample volumes will require longer extraction time and affect the stability of the microdrop. In the headspace mode, the optimized volume should be at a level which allows the microdrop to be suspended over the stirred sample, while in the direct immersion mode, the sample volume should only be enough to avoid the sample coming in contact with the septum [3, 76, 77]. The presence of air bubbles should also be avoided in the syringe to avoid errors in the analysis.

3.1. Single drop microextraction (SDME)

SDME is a microextraction technique, which is based on the suspension of a single droplet of water-immiscible organic solvents (typically 0.5–3 µL) from the tip of a microsyringe needle in an aqueous solution [12, 75], thus drastically reducing the volume of organic solvents used. The analytes are distributed between the microdrop of the solvent at the tip of the syringe and the sample solution [78]. The analyte which is extracted by passive diffusion onto the droplet is retracted back into the syringe and injected directly into the analytical instruments (GC, HPLC or CE). The evaporation and reconstitution of analytes before injection is eliminated and the technique provides highly enriched extracts of the analytes [12].

The SDME extraction can be carried out in direct immersion (in which the droplet is suspended directly into the aqueous sample), and is most suitable for the analysis of medium polar or non-polar analytes or headspace mode (where the droplet is suspended in the headspace of the sample solution) and is suitable for the analysis of volatile or semi-volatile analytes. The technique was first reported by Liu and Dasgupta, using a 1.3 µL chloroform suspended in a large aqueous solution containing a methylene blue active substance [79], and later by Jeannot and Cantwell for the extraction of 4-methyacetophenone in aqueous solution, using 8 µL of n-octane suspended at the end of a Teflon rod [80]. The extraction technique was found to be simple, flexible and can easily be coupled to chromatographic instruments. Its coupling with GC and HPLC has been reported and reviewed extensively, while it has also been successfully coupled with ICP-MS, ET-AAS, FIAAS, MALDI-MS, CE and MS [3, 81].

The use of a Teflon rod as a microdrop holder implies that extraction from the sample and injection of analytes into chromatographic instruments are performed separately with different apparatus [75, 82]. This limitation was overcome by the introduction of a microsyringe as the microdrop holder [83], and the organic solvent can be withdrawn after
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extraction and injected directly into the GC system [81]. Another limitation is the instability of the microdrop of solvent in the DI-mode at high stirring rate and long extraction times [3]. Therefore, in the development of SDME technique, there is need for the optimization of factors such as selection of extraction solvent, solvent drop volume, agitation rate, ionic strength, extraction temperature and time, sample and headspace volume and automation [76].

Few studies have been published regarding its application for the extraction of pesticide residues from fruit and vegetable samples. The techniques was used for the analysis of 20 multiclass pesticides in apple [84], and in tomato, using toluene [85, 86], analysis of triazole pesticides in water and grape juice samples, with extraction by n-hexanol/n-hexane (50:50,v/v%) [87]. The presence of organochlorine pesticides was also investigated in vegetable samples (cabbage, cauliflower and Chinese cabbage) using SDME-GC/MS using a mixture of 1 µL p-xylene/acetone (80:20, v/v %) [88] and organophosphorus pesticides in fruit juices. [89], and in apple, pear and orange juice samples [90], using toluene as the extraction solvents. Organophosphorus and organochlorine pesticides were also determined in cucumber and strawberry using toluene (1.5 µL) [91], while a mixture of octanone and undecanone was used for the extraction of oxazole fungicides from fruits samples [92]. The choice of toluene by most authors was based on the fact that it is stable, less toxic, possesses a higher extraction efficiency and its suitability for direct GC injection. All the developed methods gave comparable analytical figures of merit compared to SPME.

3.2. Hollow fiber liquid phase microextraction (HF-LPME)

HF-LPME is a multi-phased microextraction system, which was developed to enhance the stability of the organic solvent in 1999 [93, 94]. It is based on the principle of a supported liquid membrane [95], in which the organic solvent is used to fill both the wall pores and the HF lumen. It makes use of a polymeric membrane which forms a barrier between the solvent and the sample [96], and acts as a support for the small volumes of extracting solvents. It involves filling of a few microliters of solvent inside the pores and lumen of a semi-permeable polypropylene hollow fiber attached to a syringe. The HF-LPME can be carried out in either the static or dynamic mode. In the static mode, the acceptor phase is introduced in the lumen followed by the immersion of the fiber into the aqueous sample by a syringe, while in the dynamic mode the HF is attached to a syringe connected to a programmable pump [75, 78].

The extraction can be carried out in two- or three phases [95]. In the two-phase mode, the aqueous sample (donor) makes contact directly with the organic solvents (acceptor) through the membrane pores, by a repeated pushing and pulling of the microsyringe plunger [97], and the mass transfer of the analytes is driven by the diffusion of the analytes from the sample matrix into the organic solvent. When the pores are prefilled with an organic solvent, which provides a supported liquid membrane, a three-phase system is formed, and the sample solution and organic solvent are separated by the hollow fiber membrane. The solvent used must be compatible with the membrane, so as to ensure that the pores in the
wall of the membrane is completely filled [75]. The technique can also be carried out in the headspace mode, but most researchers have used the direct immersion mode for efficient pre-concentration of the analytes. The limitation of this technique is the issue of carry-over [98], therefore a new membrane should be used for each extraction.

The HF-LPME membranes are capable of accommodating larger volumes of organic solvents which increases the efficiency of the extraction, while the pore acts as a filter which prevents interference of large molecular weight molecules present in the sample matrix. The technique has not been used extensively for pesticides analysis in food samples, therefore only a few studies have been reported for its applications in fruit and vegetable samples. It has been used for extraction of pesticide residues in vegetables using dihexyl ether [99], triazines in watermelon using toluene immobilized on MIP-HF [100], fungicides from orange juice using 2-octanone [101], organochlorine pesticides from tomato and strawberry using a mixture of toluene and hexane [102] and pesticides from grapes with pressurized hot water [103]. The choice of the water-immiscible solvents was based on their ease of immobilization into the HF, with low volatility and high partition coefficients.

3.3. Dispersive liquid-liquid microextraction (DLLME)

DLLME is a microextraction technique introduced by Assadi and co-workers [104] which also makes use of microliter volume of a mixture of extraction solvent and dispersive solvent. This helps to minimize dislodgement of the organic solvent drop inherent in SDME. It involves the formation of a cloudy solution when an appropriate mixture of high density water-immiscible extraction solvent and dispersive solvents is injected rapidly into an aqueous solution [104, 105], containing the analytes of interest. The hydrophobic solutes are then enriched in the extraction solvents, which are dispersed into the bulk aqueous solution and the mixture is centrifuged, thus, making DLLME a two-step extraction technique. The extractive solvent accumulates at the bottom of the extraction vessel and can be injected with or without further treatment into analytical instruments. The choice of the type and volume of dispersive solvent is as important as that of the extraction solvent, because, it helps the extraction solvent to form fine droplets in the sample matrices. The nature of the fine droplet has been found to enhance extraction efficiency, because of the abundant surface contact between the droplet and the analytes, thus the mass transfer of analytes into the extraction solvent is speeded up [75].

The use of DLLME has also been extended to the analysis of pesticide residues in fruit and vegetable samples which resulted in efficient extraction, high enrichment factors and low detection limits. The technique was used for the analysis of multi-residue pesticides in peach juice, pulps and peels using dodecan-1-ol (4 µL) and acetone (4 µL) as the extraction and dispersive solvents respectively, and the extraction was based on floating organic solvent [106]. Organophosphorus pesticides were analyzed in orange juice samples using chlorobenzene (50 µL) and ultrasound assisted emulsification [107], also in banana using an ionic liquid ([BBIm][PF_6]) based extraction solvent and methanol (600 µL) [108], in tomato with ultrasound assisted solvent extraction followed by DLLME with chlorobenzene (10 – 11 µL) as
an extraction solvent with acetone (1 ml) as the dispersive solvent [109], and in watermelon using chlorobenzene (27 µL) and acetonitrile (2.5 ml). Carbamate pesticides were also analyzed in banana, pineapple and tomato juice using trichloromethane (800 µL) and methanol (1.5 ml) [110] and in apple using trichloromethane (60 µL) and acetone (1 ml) [111].

Neonicotinoid insecticides was also analyzed in apple using chlorobenzene (9 µL) and acetone (1 ml) [112], and in tomato and cucumber using trichloromethane (200 µL) and acetonitrile (2.5 ml) [113]. Multiclass pesticides were determined in banana [114], table grape and plum [115], using ionic liquid ([C₆MIm][PF₆]) based extraction solvent and methanol (714 µL) and in apple juice using tetrachloromethane (100 µL) and acetone (500 µL). It was also used for the analysis of triazophos and carbaryl from apple, grape and peach [116], fungicides from pear, grape and strawberry [117], imidacloprid from tomato [118], using tetrachloroethane and acetonitrile, cypermethrin and permethrin from pear juice using tetrachloroethene and methanol, diethofencarb and pyrimethanil from apple pulp and peel using 1-undecanol and acetonitrile as the extraction and dispersion solvents respectively. The technique was also found to yield a better enrichment factor and low detection limit.

4. Stir bar sorptive extraction (SBSE)

SBSE is also a microextraction technique similar to SPME but with a greater extraction capacity. It helps to overcome the small volume of the coated SPME fiber for a better enrichment factor. In the SBSE technique, a 10 to 40 mm long magnetic stir bar coated with 50 – 300 µL of polydimethylsiloxane (PDMS) is used as the extracting phase [12]. The extraction mechanisms are similar to those of SPME, but the enrichment factor, which is determined by the amount of extractive phase is higher. The analytes are adsorbed on a PDMS coated magnetic rod, by stirring the sample solution with the rod for a given time. The stir bar can then be thermally desorbed into GC or by organic solvent to be subsequently injected to an LC system [119, 120]. The limitation of this technique include the need for reconstitution in a solvent before chromatographic analysis, since the stir bar fiber cannot be directly injected into the split/splitless injection port of a GC [96, 120]. The tedious reconstitution step can lead to introduction of contaminants and loss of analyte. It also involves longer desorption time, due to the higher amount of stir bar coating.

The extraction process like SPME is dependent on the partition coefficients between the analyte and the coated stir bar. The PDMS coated fiber is commercially available, and has widely been used, while other polymeric phases such as restricted access materials, sol-gel prepared coatings and carbon adsorbents have also been recently developed. In the SBSE method development, factors such as extraction time and temperature, pH, salt and organic solvent addition, sample volume, agitation speed and volume of acceptor phase are very important and need to be optimized [96, 120] for higher extraction efficiency, recovery and low detection limit. The technique has successfully been applied for the extraction of pesticides residues in fruit and vegetable samples. An organophosphorus pesticide (OPP) was analyzed in cucumber and potato using sol-gel coating stir bar [121]. It has also been used for the extraction of multiclass pesticides in different fruits and vegetable samples [122-
124], using PDMS coated stir bar, organochlorine and organophosphorus in grape and peach juice using poly(phthalazine ether sulfone ketone) coated stir bar [125]. A method which compared SBSE and matrix solid phase dispersion was developed for the determination of multiclass pesticides in orange using PDMS coated stir bar [126].

5. Microextraction in packed solvents (MEPS)

MEPS is a recently developed microextraction technique. It is a miniaturization of conventional SPE packed bed devices from milliliter bed volume to microliter volumes, and uses the same sorbent bed integrated into a liquid handling syringe that allows for low void volume sample manipulation [127]. It can be connected online with GC or LC without any modifications, and can be fully automated [128]. The sorbent (1-2 mg) is either inserted into the syringe (100-200 µL) barrel as a plug or between the needle and the barrel as a cartridge [127, 129]. The cartridge bed can be packed or coated to provide selective and suitable sampling conditions and make use of silica based (C2, C8 C18) and strong cation exchanger (SCX), polystyrene-divinylbenzene copolymer or molecular imprinted polymer, as the extracting phase [127, 130].

The extraction technique which can be performed on-line with GC or LC involves dilution of the sample followed by drawing the sample up and down through a conditioned sorbent solid phase plug in the syringe. The solid phase is washed with water or with other solvents in the case of water soluble analytes, to remove any interfering materials and the analytes are eluted with a microliter volume of organic solvent. The technique was recently used for the analysis of multiclass pesticides in water samples [131, 132], but till today it has not been used for fruits and vegetables analysis. It presents a good and promising microextraction technique for the analysis of a broad range of pesticides in food samples. It also requires the optimization of factors such as the nature of adsorbent, nature and volume of elution solvent, nature and volume of washing solution and number of extraction cycles [127, 128, 130], to achieve an efficient extraction for better sensitivity and low detection limits.

6. Interface to analytical instrumentation

The automation of the microextraction techniques described in this review has gone a long way in increasing the efficiency and accuracy of the extraction procedures and subsequent instrumental analysis, by preventing loss of sample and introduction of other contaminants. All the techniques except SBSE have been conveniently interfaced to chromatographic analytical instruments. At present SPME offers the best technique because of its solvent-less nature, since other microextraction techniques make use of water-immiscible solvents, and the GC technique is the most preferred analytical instrument and has been used in most of the published work in microextraction analysis. The techniques have also been successfully interfaced with HPLC and CE, but only a few papers have been reported [81, 94]. The GC analysis provides higher sensitivity, selectivity and better detection limits than LC in pesticide analysis, while the CE provides a faster alternative to the chromatographic techniques but with higher detection limit [77]
7. Limitations and future trends

The use of microextraction technique is emerging as a very reliable sample preparation method, while employing little or no solvent. The advantages over the traditional method include their simplicity of operation, rapid sampling, low cost, high recovery and enrichment factor and being environment-friendly. The major limitations of these techniques include low recommended operating temperature, low volume of fiber coatings, fiber breakage and stripping of coatings in SPME, low volume of microdrop solvent, instability of the solvent, possible loss of organic solvent in SDME, the presence of porous membrane, use of a large amount of solvent for analyte elution in HF-LPME, difficulty of the automation, use of large volume of dispersive solvent and solvent dissolution in DLLME. In SBSE, the major limitations include the need to rinse, dry and reconstitute the analyte, while in MEPS, limitations include, carry-over of analytes, low enrichment factor and the presence of small amounts of water residue on the packed sorbents. The use of more selective, efficient and versatile extraction procedure and increasing interest in overcoming the aforementioned limitations and trend towards automation will provide better integration of sampling and instrumental analysis which can be used for a wide range of analytes. The limitations can also be reduced by careful optimization of all the required parameters. The use of nanoparticles as the fiber coating (SPME and SBSE)), microdrop solvents (LPME) and packed sorbent (MEPS) is a fast growing area of microextraction technique which is yet to be fully explored.

8. Conclusion

The miniaturization of sampling procedure and the need to reduce sampling time and solvent volume has led to the development of various microextraction techniques. The introduction of ionic liquid based and sol-gel prepared ionic liquid extraction phase, which can be used for all the microextraction techniques will provide a better enrichment factor, higher recovery, low detection limit and higher extraction throughput due to their unique properties such as negligible vapour pressure, good thermal stability, and high viscosity. SPME remains the most widely used technique, especially with the introduction of ionic liquid based, molecular imprinted and sol–gel prepared fiber coatings and introduction of the metal alloy fiber. However, the microextraction technique is an emerging field of study which will provide inexpensive and solvent-less analysis of a wide range of pesticide residues and other contaminants in food samples.

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