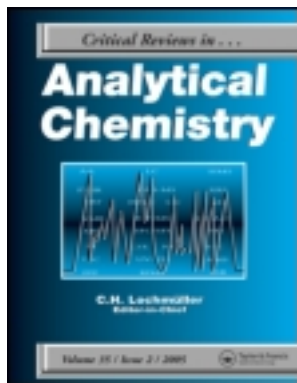


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Lukman Bola Abdulra'uf<sup>a b</sup>, Wasu Adebayo Hammed<sup>a</sup> & Guan Huat Tan<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

<sup>b</sup> School of Basic and Remedial Studies, Kwara State College of Education, Ilorin, Nigeria

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# SPME Fibers for the Analysis of Pesticide Residues in Fruits and Vegetables: A Review

Lukman Bola Abdulra'uf,<sup>1,2</sup> Wasiu Adebayo Hammed,<sup>1</sup>  
and Guan Huat Tan<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia*

<sup>2</sup>*School of Basic and Remedial Studies, Kwara State College of Education, Ilorin, Nigeria*

Food samples are usually analyzed with a preliminary step of sample preparation, because pesticide residues are present in low concentrations and embedded in complex matrixes. Solid phase microextraction (SPME) is a solvent-free extraction technique that is fast, relatively inexpensive, easily automated, and versatile with high sample throughput. Analyte extraction, pre-concentration, and introduction into the analytical instrument are achieved in a single uninterrupted process. SPME uses fibers coated with a polymeric stationary phase that can be either a solid, liquid, or a combination of both. The fiber coating extracts the target analytes from a complex food matrix by absorption in the case of liquid coatings or adsorption in the case of solid coatings. The SPME fiber is then transferred into the analytical instrument for desorption and analysis of the target analytes. The use of sol-gel technology in the production SPME coated fiber has helped to increase the range of pesticide residues that can be extracted with the SPME technique.

**Keywords** SPME, coated fiber, sol-gel, pesticide residues

## INTRODUCTION

An accurate assessment of pesticide residues and other contaminants in fruits and vegetables is very important due to increasing awareness of the effects of these chemicals on human health. The need to satisfy the drastic increase in the demand for fruits and vegetables by a growing population has led to an increase in the use of pesticides. Although the use of pesticides has helped to increase food production, it is necessary to strike a balance between their benefits and the possible risk to human health. Therefore, there is an urgent need for quality control monitoring of the use of such pesticides on fruits and vegetables for safety purposes.

The analysis of fruits and vegetables for the evaluation of pesticide residues is an important aspect of quality control measures put in place to prevent the misuse of pesticides. Although various analytical techniques have been developed for food analysis, most analytical instruments cannot handle the sample matrixes directly (Kataoka et al., 2000). However, this is not a simple task as fruits and vegetables contain a wide range of complex compounds that cause interference with instrumental analysis. Food analysis involves several steps: sampling, sample prepa-

ration, separation, detection, quantification, and data analysis, the purpose of which is to obtain information on the quality and quantity of pesticide residues present in the fruit and vegetable samples.

The sample preparation step is a most critical step in the qualitative and quantitative analysis of pesticide residues in fruits and vegetables. To achieve this, several extraction methods such as solid phase extraction, liquid-liquid extraction, supercritical fluid extraction, and pressurized liquid extraction (De Koning et al., 2009) have been developed. However, these sample preparation techniques are tedious, time consuming, and use large volumes of toxic solvents (Kataoka et al., 2000), and could also lead to loss of analytes, giving rise to analytical errors. An ideal, effective, efficient, and simple sample preparation technique should combine sample isolation, concentration and qualitative and quantitative determination of pesticide residues in a simple step, irrespective of the complexity of the sample matrixes.

Fruit and vegetable samples are usually analyzed with a preliminary sample preparation step (Ahmed, 2001), since pesticide residues are usually present at a trace concentration level, embedded in complex sample matrixes. This requires an efficient and effective extraction technique that allows for greater selectivity in the concentration of analytes, thus the need for various sample matrix pretreatment methods. The current reliable and accurate analysis of fruits and vegetables is focused on the

Address correspondence to Lukman Bola Abdulra'uf, Dept. of Chemistry, University of Malaya, Lembah Pantai 50603, Kuala Lumpur, Malaysia. E-mail: abdulraflukman@siswa.um.edu.my

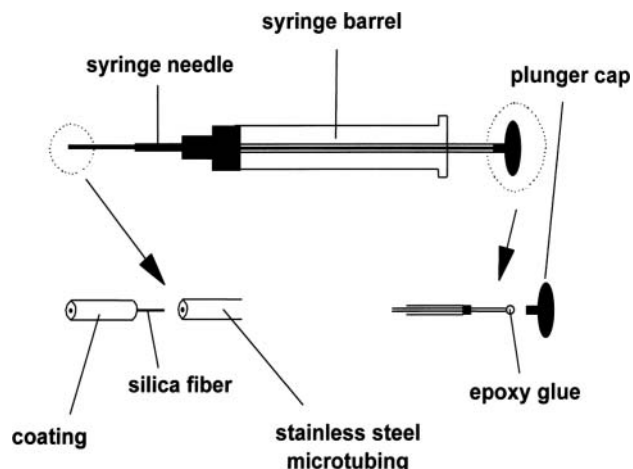


FIG. 1. Custom-made SPME on Hamilton 7000 series syringe (Lord and Pawliszyn, 2000; Pawliszyn et al., 1997). Reprinted with permission.

simplification, miniaturization, and improvement of the sample preparation steps such as extraction, concentration, analyte isolation, and cleanup (Kataoka et al., 2000; Pawliszyn et al., 1997), using microextraction methods. Solid phase microextraction (SPME) has provided a solventless alternative extraction and sample preparation method that has helped to eliminate all the limitations inherent in other traditional sample preparation techniques. It is based on the use of a fused silica fiber that is coated on the outside with a thin film of an appropriate polymerized stationary phase attached to a stainless steel rod, mounted on a fiber holder and housed in a modified syringe (Figure 1).

In this article, various types of SPME fibers used in the extraction of pesticide residues from fruits and vegetable samples are reviewed. The review also includes the SPME theory, type of SPME mode, the conditions affecting SPME fiber performance, and its advantages and limitations.

### SOLID PHASE MICROEXTRACTION (SPME)

The solid phase microextraction technique was introduced in 1989 by Pawliszyn and his coworkers (Arthur and Pawliszyn, 1990) as a solvent-free extraction technique. It was developed in an effort to address the need to facilitate a rapid, efficient, effective, and field-compatible sample preparation method (Lord and Pawliszyn, 2000; Pawliszyn et al., 1997; Risticvic et al., 2009) that eliminates the use of toxic solvents, saves preparation time, and reduces the overall cost of analysis. It offers the benefit of a short sample preparation step, solventless extraction, small sample volume, and concentration of analytes from solid, liquid, or gaseous samples. The development of SPME has helped to eliminate some drawbacks of solvent-based conventional sample preparation methods. It can easily be automated, thus integrating sampling, extraction, pre-concentration, and sample introduction into the analytical instrument in a single and uninterrupted sampling step, resulting in high throughput analysis

(Picó et al., 2007; Risticvic et al., 2009), thereby avoiding sample contamination and loss of analytes.

The SPME process involves two basic steps: the partitioning of analytes between the coating and the sample matrix, and the desorption of the concentrated extracts into the analytical instruments (Pawliszyn, 1997), without any cleanup step (Arthur and Pawliszyn, 1990). The sorption process starts by the exposure of the fiber to the vapor phase above the sample matrix or by direct immersion in the matrix. The transfer of analytes to the fiber occurs through the mass transfer process, according to the second law of thermodynamics (Nerín et al., 2009). The fiber is exposed for a given period of time, and the extraction is considered to be completed when equilibrium is attained. The SPME fiber is then transferred to a chromatography instrument for desorption, separation, and quantification of the extracted analytes. The desorption process occurs thermally in the hot injector of a gas chromatography instrument, and by a mobile phase solvent before injection into a liquid chromatography instrument.

The coupling of SPME to gas chromatography (GC) is widely used for pesticide residues analysis because it can easily be automated. High-performance liquid chromatography (HPLC) is used for analytes that are not amenable to GC, and for polar, poorly, volatile and thermally labile analytes. The use of HPLC for desorption is attractive, but usage lags due to its equilibration time, lack of commercially available interfacing options, lack of automation, and limited number of commercially available SPME sorbents for LC application (Lord, 2007; Nerín et al., 2009). Mobile phase desorption solvents reduce the fiber coating life-utility due to its possible swelling by the mobile phase organic solvent, and there is also need for modification of the LC injector. The ease of use of SPME and its simplicity makes it an improved and the most convenient extraction technique, and thus a superior alternative to conventional sample preparation methods.

### Theory of SPME

The theory of SPME has been described by Pawliszyn and his coworkers (Arthur et al., 1992; Arthur and Pawliszyn, 1990; Zhang and Pawliszyn, 1993). The theory shows that there is a partition of analytes between the SPME fiber coating and the sample matrix. Then a linear proportional relationship must exist between the amount of analyte extracted by the SPME fiber coating and the initial concentration of analyte in the sample matrix in order to achieve quantitative extraction.

### Thermodynamic Considerations

SPME extraction involves phase equilibration processes (Pawliszyn, 1997); direct immersion involves two phases (SPME fiber coating and sample matrix) and one interface (SPME fiber coating/sample matrix), while headspace involves three phases (the headspace gas, SPME fiber coating and the sample matrix) with two interfaces (SPME fiber

coating/headspace gas and sample matrix/headspace gas) (Ai, 1997a; Beltran et al., 2003).

The amount of analyte extracted from the sample matrix can be described using Nernst's partition law (Arthur and Pawliszyn, 1990). In an equilibrium situation, there exist a linear proportional relationship between the amount of analyte extracted ( $n$ ) and the initial concentration of the analyte in the sample matrix ( $C_0$ ), described by the relation  $n \propto C_0$ , for qualitative analysis (Ai, 1997b). The partition coefficient or equilibrium constant is expressed as the concentration of the analyte in the SPME fiber coating ( $C_f$ ), the concentration of analyte in the sample matrix ( $C_s$ ), and the concentration of analyte in the headspace ( $C_h$ ).

The SPME fiber coating and headspace interface distribution coefficient is defined as:

$$K_{fh} = \frac{C_f}{C_h} = \frac{(n/V_f)}{C_0 - (n/V_h)} \quad [1]$$

and the headspace and sample matrix interface distribution coefficient are defined as:

$$K_{hs} = \frac{C_f}{C_s} = \frac{(n/V_f)}{C_0 - (n/V_s)} \quad [2]$$

$$K_{fs} = \frac{C_f}{C_s} = \frac{(n/V_f)}{C_0 - (n/V_s)} \quad [3]$$

$$K_{fs} = K_{hs} K_{fh} \quad [4]$$

$V_f$  is the volume of the SPME fiber,  $V_s$  is the volume of the sample matrix, and  $V_h$  is the volume of headspace. The amount of analyte extracted by the SPME fiber coating is given as:

$$n_f = \frac{K_{fs} V_f V_s C_0}{V_s + K_{fs} V_f + K_{hs} V_h} \quad [5]$$

Equation (5) shows that the amount of analyte extracted does not depend on the location of the fiber in the sample vial. The fiber could be placed in the headspace or directly in the sample, provided the volume of the SPME fiber coating, headspace, and sample are kept constant (Pawliszyn, 1997). The denominator represents the analyte capacity for the SPME fiber coating ( $K_{fs} V_f$ ), headspace ( $K_{hs} V_h$ ), and sample matrix ( $V_s$ ) phases. In the direct immersion mode, that is, when there are two phases with one interface (SPME fiber coating/sample matrix), Equation (5) becomes

$$n_f = \frac{K_{fs} V_f V_s C_0}{V_s + K_{fs} V_f} \quad [6]$$

In many cases, the SPME fiber coating/sample matrix distribution constant ( $K_{fs}$ ) is relatively small with respect to the phase ratio of SPME fiber coating and sample matrix ( $V_f \ll V_s$ ), and if the analyte has a very high affinity for the SPME fiber coating  $K_{fs}$  will be very large and thus  $K_{fs} V_f \gg V_s$  and Equation (6) becomes

$$n_f = K_{fs} V_f C_0 \quad [7]$$

Equations (6) and (7) show that there is a direct relationship between the amount of analyte extracted ( $n$ ) and the ini-

tial concentration of the analyte in the sample matrix, and that the amount of analyte extracted by the SPME fiber coating is independent of the sample volume, provided  $K_{fs} V_f \gg V_s$ , and quantitative analysis can be achieved. The distribution constants value can be calculated from chromatographic parameters. The theoretical models show that there is diffusion of the analytes from the sample to the fiber coating, but this does not exist within the solution (Prosen and Zupancic-Kralj, 1999).

### Kinetics Consideration

The speed of an SPME process is described by the kinetics of extraction. The SPME extraction rate is determined by mass transfer and diffusive transport of analytes from the sample matrix to the fiber coating (Zhang and Pawliszyn, 1993). The theory of mass transfer of analytes to the SPME fiber coatings is based on Fick's second law of thermodynamics, which describes mass balance in a dynamic system (Pawliszyn, 1997). In headspace SPME, when diffusion of the analyte from the fiber surface to its inner layers is a slow process, it can be considered as the rate-determining step, whereas, if the evaporation of the analyte from the sample matrix to its headspace becomes the rate-determining step, the mass transfer at the headspace/fiber coating interface is considered as a relatively fast process (Ai, 1997a). The rate of extraction is inversely proportional to the diffusion coefficient of the analyte in the sample matrix and directly proportional to the square of the fiber thickness.

At the start, the concentrations of analytes in the fiber coating increase rapidly and then decrease with time until equilibrium is reached. Fibers coated with thicker films require a longer time to attain equilibrium (Kataoka et al., 2000; Prosen and Zupancic-Kralj, 1999), but more analytes will be extracted onto the fiber, resulting in higher sensitivity. The extraction kinetics is important for the optimization of the parameters that affect the efficiency of the SPME extraction, such as extraction time and temperature, agitation, and salt addition. It helps to identify its limitations and indicates strategies to increase the extraction speed (Pawliszyn, 1997, 1999). Modification of the kinetic theory is possible for extraction in a fiber coating that contains a high reagent concentration.

### Extraction Mode

There are two major types of extraction modes used in the analysis of pesticide residues in fruit and vegetable samples. These are the headspace SPME (HS-SPME) and direct immersion SPME (DI-SPME). Figure 2 (Aulakh et al., 2005; Kataoka et al., 2000) illustrates the differences between these two modes. The efficiency of extraction of each mode is dependent on the sample matrix composition and the nature and volatility of the analytes. Both extraction modes have been successfully used in the extraction of pesticide residues from fruit and vegetable samples.

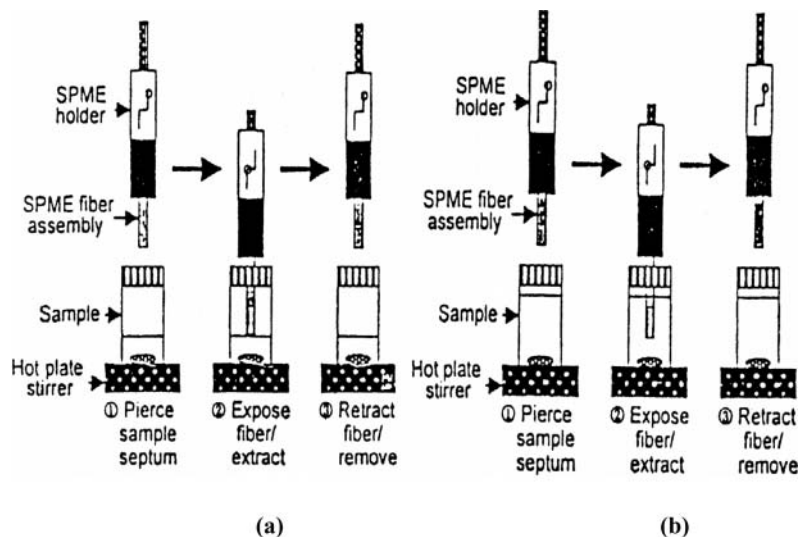


FIG. 2. (a) Headspace and (b) direct immersion SPME (Kataoka, et al., 2000). Reprinted with permission.

#### Headspace Solid Phase Microextraction (HS-SPME)

In the HS-SPME mode, the fiber is exposed to the vapor phase above a gaseous, liquid, or solid sample. The analyte is transported through a layer of gas before reaching the fiber coating (Kataoka et al., 2000; Lord and Pawliszyn, 2000), where the fiber coating extracts the analyte from the headspace, equilibrated with the sample matrix (Pawliszyn, 1999). Headspace sampling helps to prolong the fiber coating life by protecting it from damage by high molecular weight substances present in the sample matrix. Extraction in the headspace mode allows for the modification of the sample matrix-related extraction parameters, such as pH and salt concentration, without any effect on the fiber and reduces the extraction rate.

The analytes are extracted indirectly from the sample matrix, therefore more volatile components that are at higher concentration in the headspace are extracted faster than the less volatile components embedded in the sample matrix (Pawliszyn et al., 1997). Extraction efficiency in the headspace mode is enhanced by increasing the temperature of the sample matrix, and this leads to an increase in the diffusion coefficient of the analytes (de Fátima Alpendurada, 2000). An increase in extraction temperature beyond the optimized conditions also leads to reduction of the distribution constant; this effect could be overcome by the use of internally cooled fiber (Chai and Tan, 2009; Chai et al., 2008a; Pawliszyn, 1997). Sampling of volatile analytes from a complex matrix is usually done in the headspace mode.

#### Direct Immersion Solid Phase Microextraction (DI-SPME)

This extraction mode involves the insertion of the coated fiber into the sample matrix, where transport of the analytes from the sample matrix to the coated fiber is achieved (Lord and Pawliszyn, 2000). Rapid extraction in the aqueous phase is facilitated by some degree of agitation, such as forced flow, vial

or fiber movement, stirring or sonication (Lord and Pawliszyn, 2000; Pawliszyn et al., 1997) to increase the rate of transport of analytes to the fiber coating vicinity, which are subsequently taken up by the fiber. This reduces the sample matrix diffusion layer and the effects caused by the depletion zone near the coated fiber as a result of slow diffusion in the solution and fluid shielding.

#### SOLID PHASE MICROEXTRACTION (SPME) FIBER

The SPME fiber is a fiber coated with a liquid polymer, solid sorbent, or a combination of both (Kumar et al., 2008). Several SPME fiber coatings have been developed for the extraction of various classes of pesticide residues in fruit and vegetable samples. The effectiveness and efficiency of the technique depend on the type, thickness, and coating volume of the fiber (Lord and Pawliszyn, 2000; Wardencki et al., 2004). The sensitivity is dependent on the distribution constant of the analytes partitioning between the sample matrix and the fiber coating. The distribution constant describes the properties of a fiber coating and its selectivity and specificity for the extraction of the pesticide residues against other complex components present in the fruit and vegetable matrixes. Therefore, appropriate fiber coatings are selected based on their nature and volatility and their affinities to the pesticides. Thicker fibers are used for volatile pesticides, while thin fibers are suitable for pesticides with higher boiling points.

There are different methods for the preparation of SPME fiber coatings. There is the dipping technique that consists of placing a fiber in a concentrated organic solution of the polymerized material for a short time. The fiber is then removed and evaporated by drying and the deposited fiber is then cross-linked. The other method, electrodeposition, which is an extension of the previous method, involves the selective deposition of the coating materials on the surface of a metallic rod (Zhang et al., 1994). The

difference in coating thickness from fiber to fiber is a limitation of this fiber preparation method (Lord and Pawliszyn, 2000) and is overcome by simultaneously depositing the coating during the drawing of the fused-silica rod. Another method includes drawing the fiber by means of a fiber optic tower, which involves melting of a fused-silica rod and drawing it into a thin rod. The drawn fiber is then allowed to cool at room temperature and then passed through an applicator containing a concentrated solution of the coating material in an organic solvent (Mani, 1999).

Sol-gel technology-derived fibers are produced using an appropriate precursor. It involves the removal of the protective polyimide layer of the fused-silica fiber by dipping, after which it is dipped in NaOH (Kumar et al., 2008; Zeng et al., 2008). The fused-silica is then dipped into a sol solution containing the appropriate precursor. The sol-gel preparation involves the use of a precursor, usually a metal alkoxide,  $M(OR)_x$ , a hydroxyl-terminated sol-gel active polymer, solvents to disperse the precursors, an acidic or a basic catalyst, and water (Kumar et al., 2008).

### Commercial SPME Fiber

There is need for proper selection of fiber coating in order to achieve efficient extraction of the target analyte from the complex sample matrix. Several commercial SPME fibers are available with different fiber coatings, volume, thickness, and phase mixtures. They are designed to be used by manual (Figure 3) or automated sampling. The coatings on the fused-silica fibers can be non-bonded, bonded, partially cross-linked, or highly cross-linked (Kataoka et al., 2000; Krutz et al., 2003). There are seven commercially available SPME fibers, two with homogeneous and five with mixed phase coatings.

The homogeneous polymer coatings extract via absorption with the analyte diffusing into the bulk of the coatings. Poly-

dimethylsiloxane (PDMS) is a nonpolar homogeneous fiber, manufactured in three different film thicknesses, 7, 30, and 100  $\mu\text{m}$ , and in two forms, bonded and non-bonded (Mani, 1999). PDMS is the most commonly used SPME fiber coating for the extraction of pesticide residues from fruit and vegetable samples. The PDMS fiber is preferred for the extraction of nonpolar pesticides. However, it has widely been used for the extraction of more polar pesticides, after the extraction conditions have been optimized. PDMS fiber is very rugged and can withstand high injector temperatures up to about 300°C (Kataoka et al., 2000). PDMS was found to have low affinity for polar pesticides, thus polar SPME was developed. Polyacrylate is also a homogeneous fiber, which is available in 85  $\mu\text{m}$  thickness. It is a partially cross-linked solid crystalline coating and more polar. Its polarity makes it suitable for the extraction of polar pesticides.

The mixed fiber coatings containing fibers are coated with different porous particles embedded in partially cross-linked polymeric phases. The mixed coatings PDMS/divinylbenzene (DVB), DVB/PDMS/carboxen (CAR), carbowax (CW)/PDMS, CW/DVB, and CW/template resin (TPR) extract by adsorption and have complementary properties of each constituent polymeric coating. They are of lower mechanical stability than the homogeneous coating, but have increased retention capacity, high distribution coefficient, smaller diffusion coefficient, and high selectivity (de Fátima Alpendurada, 2000; Mani, 1999). This is attributed to their mutually potentiating adsorption capacity.

PDMS fiber is the most frequently used fiber for the extraction of different classes of pesticide residues from fruit and vegetable samples. The 100  $\mu\text{m}$  PDMS was used by Chai et al. (2008b) for the extraction of multi-residue organochlorine and organophosphorous pesticides from cabbage, tomato, and guava in the HS mode and from strawberry, guava, bok choy, tomato,

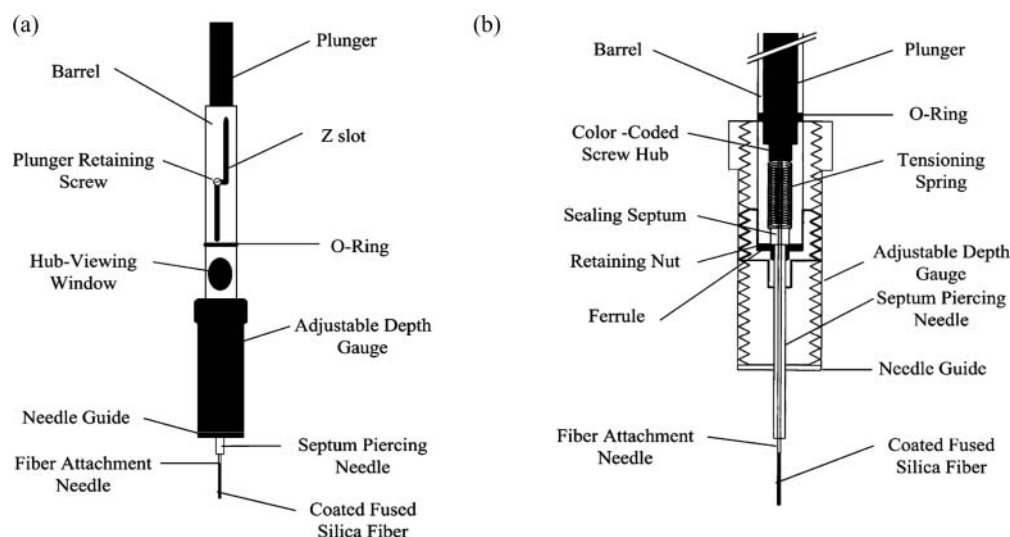


FIG. 3. Commercial SPME device: (a) SPME fiber holder and (b) cross section of SPME fiber assembly (Supelco Data Sheet No. T713019A, 1998).

star fruit, and cucumber in the HS mode (Chai and Tan, 2009; Chai et al., 2006). Organochlorine, organophosphorous, and carbamate pesticides from tomato and cucumber in the DI mode were also investigated (Chai et al., 2008c). Organophosphorous pesticides were extracted from pears and apples in the DI mode (Simplicio and Boas, 1999), from strawberries, cherries, and cherry juice in the HS mode (Lambropoulou and Albanis, 2002, 2003), from *C. coronarium* in the DI mode (Chen et al., 1998), and from 13 different vegetables in the HS mode (Fytianos et al., 2007) using 100  $\mu\text{m}$  PDMS. Twenty-five multiclass pesticides were also extracted from tomatoes in the DI mode with 100  $\mu\text{m}$  PDMS (Guillet et al., 2009). A pre-extraction method involving the use of matrix-assisted extraction followed by SPME extraction using 100  $\mu\text{m}$  PDMS was developed. The method was used for the extraction of organophosphorous pesticides from strawberries, tomatoes, and bok choy in the HS mode (Chen et al., 2002) and extraction of pyrethroid pesticides from strawberries in the DI mode (Sanusi et al., 2004). The 100  $\mu\text{m}$  PDMS was selected for the extraction after careful and effective optimization of factors (extraction time, extraction temperature, pH, salt addition, dilution, desorption time, and temperature) that affect extraction efficiency. The 100  $\mu\text{m}$  PDMS gave better extraction efficiency, good linear range, lower detection limit, and good recovery with relative standard deviation lower than 10%.

The 65  $\mu\text{m}$  PA fiber was employed for the extraction of 54 multiclass pesticides from oranges and peaches in the DI mode (Cortés-Aguado et al., 2008). The fiber coating was used for the extraction of phenyl urea pesticides from carrots, onions, and potatoes in the DI mode (Berrada et al., 2004), organophosphorous pesticides from oranges, grapes, and lemon juice in the DI mode (Zambonin et al., 2004), triazole from strawberries in the DI mode (Zambonin et al., 2002), 14 multiclass pesticides from mangoes in the DI mode (Menezes Filho et al., 2010), while 80  $\mu\text{m}$  PA fiber was used for the extraction of strobilurin fungicides from grape ketchup, strawberries, and tomatoes in the HS mode (Navalon et al., 2002).

Mixed phase coating fibers have also been used extensively for the extraction of multi-residue pesticides from fruits and vegetables in the DI mode after the optimization of dilution factors. The most widely used is 65  $\mu\text{m}$  PDMS/DVB fiber. It was employed in the extraction of pyrethroid pesticides from tomatoes and strawberries (Beltran et al., 2003), 70 multiclass pesticides from cucumbers, peppers, and tomatoes (Cortés-Aguado et al., 2007). The 60  $\mu\text{m}$  PDMS/DVB fiber was employed for the extraction of 25 multiclass pesticides from tomatoes (Guillet et al., 2009), carbamate pesticides from strawberries (Wang et al., 2000) and apples (Hu et al., 2008), pyrethroid pesticides from cucumbers and watermelons, and 7 multiclass pesticides from tomatoes (Ravelo-Perez et al., 2008). Less frequently used fibers in the extraction of pesticides from fruit and vegetable samples include 65  $\mu\text{m}$  CW/DVB, which was used for the extraction of carbamate pesticides from apples and grape juice (Natangelo et al., 2002), 50  $\mu\text{m}$  CW/TPR, used for the extraction of postharvest fungicides from cherries, oranges, and peaches

(Blasco et al., 2003), and activated carbon/polyvinylchloride (AC/PVC), used for the extraction of organophosphorous pesticides from grapes (Farajzadeh and Hatami, 2004). The extractions gave good repeatability and reproducibility with better efficiency than the single-phase coated fibers.

Limitations in the use of commercial SPME fibers include their limited range of polarity, instability at high temperatures, swelling in organic solvents, breakage of fiber, bending of needles, and stripping of coating material (Mani, 1999; Nerín et al., 2009). These drawbacks have been shown to affect the limit of desorption temperature, direct extraction from complex matrices, and automation for liquid chromatography.

### Sol-Gel Fibers

The sol-gel technology for the production of SPME fiber coatings was introduced to address the limitations observed in commercial SPME fiber coatings. It is a simple and effective method for the synthesis of materials used for SPME fiber coating. It provides a new approach for the efficient combination of organic compounds into inorganic polymeric structures in solution. Organic-inorganic materials are produced, under extraordinarily mild thermal conditions, using an appropriately designed sol solution (Chong et al., 1997; Kumar et al., 2008). The sol-gel process is an acid-catalyzed reaction that involves hydrolysis and alcohol or water condensation of the precursors and hydrolytic poly-condensation reactions of the hydrolysis and condensation products, carried out in a sol solution. It provides a greater surface area and higher thermal stability for SPME fiber coatings (Nerín et al., 2009). It does not lose its sensitivity and selectivity in organic solvents and can withstand high and low pH values of the complex sample matrix contained in fruit and vegetable samples. The efficiency of the sol-gel fiber coatings is dependent on the reaction conditions, such as temperature, nature of the precursor, solvent concentration, and type of catalyst. The most widely used catalyst is trifluoroacetic acid (TFA) containing 5% water.

Its advantages over commercial SPME fiber coatings are better homogeneity and purity, low preparation temperature, particle size control, low cost, ability to achieve molecular level uniformity, strong bonding of the coating to the substrate (silica-gel), and enhanced stationary phase stability (Chong et al., 1997; Kumar et al., 2008). It has been shown that sol-gel fibers possess a significantly higher thermal stability ( $> 320^\circ\text{C}$ ) than commercial SPME fibers, due to the strong chemical bonding between the sol-gel generated organic-inorganic composite coating and the silica surface (Chong et al., 1997). These properties allow the efficient desorption of less volatile and nonvolatile analytes and prevent carry-over, thereby extending the range of pesticide residues that can be handled by its automation to the GC technique and a longer lifetime.

A sol-gel fiber method for the extraction of organochlorine pesticides and their metabolites from radishes was developed by Dong and his coworkers (Dong et al., 2005). The sol-gel

5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxy calix[4]arene/hydroxyl-terminated silicone oil-coated SPME fiber (C[4]/OH-TSO) was prepared with tetraethoxysilane as the precursor and poly(methylhydrosiloxane) was used as the deactivating reagent. The extraction method gave a lower detection limit and better reproducibility than the 100  $\mu\text{m}$  PDMS fiber.

A sol-gel polydimethylsiloxane-2-hydroxymethyl-18-crown-6 (PDMS/2HOMe18C6)-coated SPME fiber, prepared in-house in three different compositions using methyltrimethoxysilane and poly(methylhydrosiloxane) as the precursor and deactivating agent respectively, was used for the extraction of organophosphorous pesticides from strawberries, green apples, and grapes in the HS mode. The method gave a good linear range (0.005–0.7  $\mu\text{g/g}$ ) with coefficients greater than 0.999, and a good efficiency in terms of recovery (98.7–100%) and RSD (4.2–5%) (Wan Ibrahim et al., 2010).

Cai and coworkers (Cai et al., 2006) developed a method that involves the use of three kinds of vinyl crown ether sol-gel fibers (80  $\mu\text{m}$  4'-allyl dibenzo-18-crown-6 (DB18C6), 80  $\mu\text{m}$  3'-allyl benzo-15-crown-5 (B15C5), and 84  $\mu\text{m}$  allyloxy ethoxymethyl-18-crown-6 (PSO18C60)/hydroxyl-terminated silicone oil OH-TSO) with different cavity and benzyl substitutions, cross-linked with a precursor (vinyl triethoxysilane) and a radical initiator. The fibers were optimized separately for the extraction of organophosphorous pesticides from apples, tomatoes, and apple juices in the HS mode and were compared to commercially available SPME fibers (65  $\mu\text{m}$  PDMS/DVB and 85  $\mu\text{m}$  PA). The 80  $\mu\text{m}$  B15C5/HO-TSO sol-gel-coated SPME fiber had better efficiency than the other sol-gel fibers and the commercial fibers. The extraction linear range was between 0.01 and 100 ng/g with coefficients greater than 0.99 for all pesticides investigated. The recovery value was between 70.5 and 106.4% and RSD value was 3.3–10.1%. Crown ethers are widely used due to their cavity structure and the strong electronegative effect provided by the heteroatoms in the cavity ring (Cai et al., 2006).

A method for the preparation of sol-gel-coated fiber for the extraction of organophosphorous pesticides from orange juice and bok choy was developed. Allyloxy bisbenzo-16-crown-5-trimethylsilane was used as the precursor to produce bisbenzo-16-crown-5-ether/hydroxyl-terminated silicone oil (B16C5/HO-TSO) SPME coated fiber. The sol-gel fiber showed higher efficiency with higher sensitivity for organophosphorous pesticides. The limit of detection was in the range of 0.003–1.0 ng/g (Yu et al., 2004).

An approach for the preparation of the precursor hydroxyl-terminated polymethylphenylsiloxane (PMPS-OH) has been proposed. The precursor was used for the synthesis of sol-gel PMPS-coated fiber in the presence of methyltrimethoxysilane as deactivating agents. The prepared fiber was employed in the extraction of organochlorine and organophosphorous pesticides from celery cabbage, garlic, and cabbage using the DI mode. The extraction efficiency of the sol-gel-coated fiber was found to be higher than that of commercial fibers (100  $\mu\text{m}$  PDMS, 65  $\mu\text{m}$  PDMS/DVB, and 85  $\mu\text{m}$  PA) for the investigated analytes.

The extraction linearity was from 0.5 to 1000 ng/g with coefficients greater than 0.990, and pesticide recovery ranged from 42.9 to 105.3% with RSD less than 16.2% (Zeng et al., 2008).

Factors affecting the extraction of pesticide residues from fruits and vegetables and other food samples include choice of fiber coatings, extraction mode, extraction time, extraction temperature, salt addition, sample volume, solvent addition, dilution, sample agitation, desorption time, and desorption temperature. All these conditions must be optimized for effective extraction and subsequent chromatographic determination of the target analytes. The factors have been extensively described in other review articles (Aulakh et al., 2005; de Fátima Alpendurada, 2000; Kataoka et al., 2000) as they affect extraction efficiency.

### ADVANTAGES AND LIMITATIONS OF SOLID PHASE MICROEXTRACTION (SPME)

The SPME extraction technique has also been applied for the extraction of pesticides and other contaminants from a wide range of matrixes including those found in environmental studies, industrial wastes, process monitoring, drugs, crime and forensics, and food and water analysis. The technique is frequently selected for the qualitative and quantitative sample preparation method for chromatographic analysis (GC, GC-MS, GC-MS/MS, LC-MS, LC-MS/MS) and HPLC/DAD/MS.

#### Advantages of SPME

The numerous advantages of selecting the SPME technique for pesticide residue analysis include (Hübschmann, 2009; Kumar et al., 2008; Pawliszyn, 1997; Wardencki et al., 2004):

- No toxic solvents involved
- Short sample preparation time
- Compatible with analyte separation and detection with chromatographic instruments and amenable to automation
- Allows the extraction of polar, semi-polar, and nonpolar pesticides and other food contaminants from solid, liquid, or gaseous sample matrixes
- Gives linear results for a wide range of analytes
- Better consistency and highly quantifiable results from very low analyte concentrations
- Allows for the use of small volumes of sample
- Cost of analysis is relatively low
- A small size, which makes it convenient for designing portable field-sampling devices
- Ruggedness

#### Limitations of SPME

The most important limitation is the fragility of the fiber, which has to be handled with care to avoid breakage. The quality of the needle also depends on the manufacturer, and in some cases the performance is different from batch to batch. A new

fiber has to be conditioned before use, but some bleeding of the fiber coating can sometimes occur even after careful conditioning. The GC injector temperature should always be maintained below the maximum operating temperature of the coating as specified by the manufacturer (de Fátima Alpendurada, 2000; Prosen and Zupancic-Kralj, 1999). After desorbing the analytes into chromatographic instruments, some may be carried over by the fiber, and therefore there is a need to run blank analysis with the fiber after each sampling is performed. The fiber may be permanently damaged due to the irreversible adsorption of high molecular weight compounds. Some of these limitations can be overcome by the use of headspace SPME and the introduction of the sol-gel fiber.

## CONCLUSION

Solid phase microextraction remains the best environmentally friendly sample preparation and extraction technique because of its solventless nature. Due to its ease of automation, less volatile analytes, which are not amenable to GC, can be easily quantified with HPLC because the extraction step is the same irrespective of the chromatographic instrument. Food analysis is very important for quality monitoring, control, and assurance. Therefore, the SPME sample preparation described in this review has been shown to be very effective, efficient, rapid, and versatile for the analysis of pesticide residues and contaminants from fruits and vegetables and from other food samples. The sol-gel technology approach holds considerable advantages and promises to be an edge for the development of SPME fiber coatings that can be used for a variety of analytes.

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