

Applications of Solid-Phase Microextraction for the Analysis of Pesticide Residues in Fruits and Vegetables: A Review

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This paper reviews the application of various modes of solid-phase microextraction (SPME) for the analysis of pesticide residues in fruits and vegetables. SPME is a simple extraction technique that eliminates the use of solvent, and it is applied for the analysis of both volatile and nonvolatile pesticides. SPME has been successfully coupled to both GC and LC. The coupling with GC has been straightforward and requires little modification of existing equipment, but interfacing with LC has proved challenging. The external standard calibration technique is widely used for quantification, while standard addition and internal or surrogate standards are mainly used to account for matrix effects. All parameters that affect the extraction of pesticide residues from fruits and vegetables, and therefore need to be optimized, are also reviewed. Details of the characteristics of analytical procedures and new trends in fiber production using sol-gel technology and molecularly imprinted polymers are discussed.

A nutritious, balanced diet plays a vital role in human health and well-being. Fresh fruits and vegetables constitute an important part of a balanced diet, as they contain a significant amount of nutrients and minerals (1). The production of fruits and vegetables in large quantities involves the use of toxic pesticides, and the increase in world population has led to greater demand for food production. This, in turn, has led to the introduction of pesticides, which are used to protect plants before and after harvest. The continuous use of pesticides has contributed to the steady increase in food production (2). Use of pesticides plays a beneficial role in providing large quantities of a low-cost supply of fruits and vegetables (3), but also comes with side effects.

Pesticides, including insecticides, herbicides, and fungicides, have been used effectively to control pests, fungi and weeds. Pesticides may penetrate the tissues of fruits and vegetables, where they remain as residues, result in the contamination of foods, and pose a potential risk to human health due to their

toxicity. Therefore, there is a need to strike a balance between their expected benefits and possible risks (4). Hence, their concentration must always be minimal in fruits and vegetables and must be below the maximum residue limits. Today, the monitoring of pesticide residues in food is a priority objective in pesticide research in order to allow extensive evaluation of food quality and contamination. Therefore, the analysis of pesticide residues in fruits and vegetables is essential for monitoring and safety purposes.

The purpose of any analytical study is to obtain information about substances. Analytical process involves several steps: sampling, sample preparation, separation, quantification, and data analysis (5). Sample preparation is a crucial step and, indeed, is the bottleneck of analytical methodologies in the analysis of fruits and vegetables for pesticide residues, volatile compounds, contaminants, flavors, and food additives. The current trend aimed at reliable and accurate analysis of fruits and vegetables is to focus on the simplification, miniaturization, and improvement of sample preparation, such as extraction, concentration, isolation of analytes, and cleanup (6,7), with microextraction methods. Fruit and vegetable samples are usually analyzed with a preliminary step of sample preparation, since contaminants are present at trace concentration levels (usually $\mu\text{g/g}$ or less) in complex matrixes. The analysis usually requires various matrix pretreatment methods (8), such as liquid-liquid extraction, SPE, supercritical fluid extraction (9,10), matrix solid-phase dispersion (11), and accelerated solvent extraction (12).

Solid-phase microextraction (SPME) is a solvent-free sample preparation technique (13) developed by Pawliszyn and his coworkers in 1990. Its application has been examined (14), optimized, automated (15), and reviewed (7,16,17). It is a simple and effective sorption (adsorption/absorption) and desorption technique that eliminates the need for solvents and combines sampling, isolation, concentration, and enrichment in one step (18–20). It was developed to overcome the problems associated with solvent-based, time-consuming techniques, usually multistep techniques that require the use of large volumes of samples and solvents, which cause environmental pollution and health hazards.

This article reviews various aspects of the SPME technique used in the analysis of fruits and vegetables. The review includes modes and types of SPME, including fiber types, optimization of extraction conditions, calibration methods, and the various

Guest edited as a special report on "Methods of Pesticide Residue Analysis" by Tomasz Tuzimski.

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DOI: 10.5740/jaoacint.SGE_Abdulrauf

analytical instruments used in the application of the technique for pesticide residue analysis in fruits and vegetables.

General Description of SPME

SPME saves preparation time and reduces the overall cost of analysis. Its development has addressed the need for rapid sample preparation (21). It offers the benefits of short sample preparation time, solvent-free extraction, small sample volumes, and analyte concentration from solid, liquid, or gaseous samples. It has helped to address some of the drawbacks of conventional sample preparation methods and can easily be automated, resulting in high-throughput analysis (21). Due to its remarkable analytical characteristics including linearity, reproducibility, repeatability, and low LOD, SPME is an efficient and effective extraction technique in the analysis of pesticide residues in fruits and vegetables.

SPME is a very attractive alternative technique in sample preparation that results in high selectivity, sensitivity, and versatility with minimum matrix interferences (22, 23). It has improved detection limits (18) and wide applications for the analysis of volatile and semivolatile organic compounds (24) when combined with GC/MS, and for thermally labile, polar, and nonvolatile compounds (17, 25) when coupled to LC (26) and capillary electrophoresis (CE; 27). SPME uses a chemically inert fused-silica optical fiber or metal alloys coated on the outside with a thin film of sorbent (15) as the extraction stationary phase, containing a polymeric organic compound, e.g., carbowax (CW), divinylbenzene (DVB), polydimethylsiloxane (PDMS), polyacrylate (PA), or carboxen (CAR), or a mixture of polymers (5, 6, 28), that are permanently attached to a stainless steel rod. The fiber holder consists of a spring-loaded plunger, a stainless barrel, and an adjustable depth gauge with a hollow septum-piercing needle (6) housed in a modified syringe (29, 30).

SPME is based on analyte partition and establishment of equilibrium between the analyte in the sample and the stationary phase of the coated fused silica, which can either be liquid or solid particles suspended in liquid polymer or a combination of both (15, 17, 25). The attainment of equilibrium depends on the partition coefficient (25), which reflects the chemical composition of the extraction phase and, hence, its selectivity towards a given analyte. The partition coefficient is expressed as the ratio of the concentration of the analyte in the stationary phase to its concentration in the sample. There are two distinct steps in SPME: (1) partitioning of the analytes between the extracting stationary phase and the sample matrix in the direct immersion (DI) mode and partitioning among the fiber, headspace (HS), and sample matrix in the HS mode; and (2) the desorption of the concentrated extract (21), thermally when coupled to GC or with a mobile phase solvent when coupled to LC.

SPME Methods

Fiber SPME

Fiber SPME is an extraction method in which the fiber is exposed to the analyte sample contained in a vial sealed with a septum-type cap (6). The SPME needle is pierced through the septum, and the fiber is exposed to the analyte sample for

a predetermined time (31) during which partitioning occurs between the sample matrix and the extracting stationary phase (32). The extraction process is controlled by diffusion of analytes from the surrounding solution into the fiber, through the boundary layer between the solution and the fiber, where equilibrium is established. There is maximum sensitivity at equilibrium, when a proportional relationship is obtained between the amount of analyte extracted by the fiber and its initial concentration in the sample matrix. (33). For this reason, SPME analysis does not require full equilibration for quantitative analysis (6). The extraction can be considered to be complete when distribution equilibrium of the analyte concentration is reached between the sample matrix and the fiber coating (34). At this stage, the concentration of analyte extracted remains constant and does not change with time within experimental error.

There are three different modes of fiber SPME: DI-SPME, HS-SPME, and membrane protection (31). DI-SPME (28–30, 35–37), HS-SPME (2, 14, 23, 38–46), and solvent extraction prior to DI- or HS-SPME (26, 35, 36, 47–53) are widely used for the extraction of pesticide residues from fruits and vegetables.

In the HS sampling mode, the analyte is transported through a layer of gas before reaching the coating. HS-SPME involves exposure of the fiber to the vapor phase above a liquid or solid sample (6), where the analytes are extracted from the gas phase equilibrated with the sample matrix (24). This method helps to protect the coated fiber from the effects of any nonvolatile high MW compounds in the sample matrix, which binds irreversibly to the coating and often causes interference in the extraction process. In DI-SPME, the coated fiber is inserted into the samples, where the transport of the analyte from the sample matrix into the extracting phase is achieved (31). The extraction from an aqueous sample is improved by agitation of the sample, which is done to reduce the effects of fluid shielding and reduce the sample matrix diffusion layer (7), thereby increasing the diffusion coefficients of analytes in the zone closer to the fiber (22). Effective agitation techniques, such as fast sample flow, rapid fiber or vial movement, stirring, or sonication, are used to reduce the effect of the boundary layer.

In HS-SPME there are three phases: the sample matrix, the HS gas, and the SPME polymeric fiber coating (30, 33), with two interfaces (gas/polymer and sample matrix/gas), whereas only two phases are involved in DI-SPME: the coated fiber and the sample solution, with a single interface. Membrane-protected SPME is widely used for polluted and dirty aqueous samples, for the extraction of low volatility analytes (54), and to protect the fiber. It involves two processes occurring simultaneously: extraction of analytes from the aqueous sample matrix by the porous membrane materials and subsequent extraction of the analytes from the membrane through stripping phases (55). HS-SPME helps to shorten extraction time, due to the increased rate of diffusion of analytes in the gaseous phase rather than in the liquid phase (42), and it reduces matrix effects (44), which would allow for various modifications of extraction conditions such as pH and salt addition without any effect on the fiber efficiency. Besides the DI-SPME and HS-SPME, some authors also combine other techniques prior to the SPME extraction, such as microwave-assisted extraction (MAE; 26, 52, 53).

The efficiency of extraction in the HS mode may be increased by an increase in the temperature of the sample matrix; this enhances the diffusion coefficient of the analytes and consequently reduces the distribution constant (22). This

opposing effect of temperature, that is reduction in distribution constant, was overcome by the development and optimization of circulating cooling (CC; or cold fiber) HS-SPME (18,46), which increases mass transfer and simultaneously increases the distribution constants of the analyte (21, 22). The CC-HS-SPME method allows for the simultaneous heating of the sample solution and cooling of the fiber coating, leading to an increase in the efficiency of the extraction process. There is a direct relationship between the amount of analyte extracted by the fiber and the concentration of analyte in the sample matrix (15, 33), independent of the fiber location (22). Therefore, the amount of analyte extracted into the coating from the sample solution at equilibrium is the same for DI- and HS-SPME (31). This is because equilibrium concentration does not depend on the location of the fiber provided the sample vial and gaseous HS volume are the same and remain constant.

Extraction of analytes from the sample matrix by the SPME fibers in fruit and vegetable analysis involves both mass transfer and diffusion. Either of the two processes can be the rate determining step (33), but in dynamic SPME, mass transfer is considered as the rate determining step either in HS-SPME or DI-SPME.

In-Tube SPME

In-tube SPME is an extraction technique developed for coupling to HPLC or LC/MS (6), and it is based on an open tubular capillary column that is housed in a needle (56). It consists of a piece of a fused-silica capillary column that is coated internally by a thin film of stationary extraction phase or a capillary packed with an extracting phase dispersed on an inert supporting material (31). It is easily automated with LC and can simultaneously perform continuous extraction, desorption, and injection, where the extracted analyte is desorbed into the chromatograph by a moving stream of solvent or static desorption solvent.

In-tube SPME has two approaches depending on the capillary tube used for the extraction. Dynamic in-tube contains an open-tubular fused-silica capillary column, and analytes are directly extracted and subsequently concentrated in the stationary phase of the column (57). Static in-tube SPME involves the extraction of analyte through the static gas phase present in the needle. In this technique the extracting phase is not directly exposed to the sample but is contained in a protective tubing, and it does not involve any flow of the sample through the extracting phase (31). Analytes are continuously desorbed from the fiber by the mobile phase in a dynamic mode, while desorption takes place in a small volume of solvent inside the desorption chamber in the static mode (36). When the extraction process reaches equilibrium or a sufficient extraction is achieved, the extracted analytes are directly desorbed from the stationary phase by mobile phase flow or by aspirating a desorption solvent (6). The in-tube SPME has been applied to the determination of several pesticides in aqueous samples, but its use for the analysis of fruits and vegetables (40) samples is limited.

Optimization of SPME Extraction Conditions

There are different parameters that influence the partitioning of the analytes between the sample matrix and the SPME fiber. When considering the optimization of parameters for fruit and

vegetable analysis, the complex nature of the sample should be taken into consideration. The amount of analytes extracted from fruit and vegetable samples depends on the nature of the stationary phase (fiber) and on the properties of the sample matrix. The most important method used in the optimization of extraction parameters is the consideration of the thermodynamic and theoretical models (55) in the selection of a particular procedure for the development of methods for the determination of pesticides in fruit and vegetable samples.

The optimization of the SPME conditions for fruit and vegetable samples involves selection of the extraction mode, fiber coating, extraction and desorption time and temperature, agitation, salt addition, pH, dilution, and solvent effect (6, 58). All these conditions are developed, optimized, and validated for effective extraction and quantification of pesticide residues from complex fruit and vegetable matrixes because the extraction step largely determines the figures of merit of an analytical methodology (59), such as sensitivity, repeatability, reproducibility, accuracy, LOD, LOQ, and linearity in pesticide analysis.

Extraction Modes

Selection of the extraction mode depends on the nature and properties of the sample matrix and the volatility of the pesticides. Extraction of less volatile compounds is achieved by DI-SPME, while sampling of more volatile analytes from a complex matrix is mostly done in the HS-SPME mode (6). HS-SPME also allows for variation of sample matrix properties without any effect on the fiber. In DI-SPME, matrix effects are reduced by dilution with distilled water (28, 43, 46, 60). The extraction efficiency can also be improved by previous extraction of the analyte into water or other solvent (26, 35, 36, 47–52), using focused MAE (FMAE) followed by DI-SPME. This is done due to the complexity of fruit and vegetable matrixes. Using HS-SPME results in a higher peak area and efficient extraction of the analyte in the sample compared to DI-SPME (37), reduces the extraction time, and increases the fiber lifetime. SPME in combination with GC has been found to have low affinity for the extraction of less volatile or thermally labile analytes (6), but its automation with LC has been used to overcome this setback.

Fiber Coating

The sensitivity and efficiency of SPME in the extraction of pesticide residues from fruit and vegetable samples depend on the distribution constant between the stationary phase and the sample matrix. The distribution constant describes the fiber coating properties and its selectivity (31) towards a given analyte in the presence of other matrix components. The fiber affinity for the analyte is based on the principle of “like dissolves like” (6). The efficiency of extraction depends on the type of fiber as well as the coating volume (31,58); although it takes a longer time to attain equilibrium in thicker fiber coating, it allows the extraction of a larger quantity of analytes. Thicker fibers are used for volatile pesticides, while thin fibers are suitable for pesticides with high boiling points to ensure fast diffusion and quick release into the desorption chamber of the chromatograph.

Proper selection of the fiber is necessary to achieve an

efficient extraction of target analytes from complex sample matrixes. Different fibers are used to extract different classes of pesticides. Several fibers with different coatings and thicknesses are commercially available. Sol-gel technology has been used to prepare refined, tuned coatings for specific applications (37, 39, 46, 61–64), and a molecularly imprinted polymer (MIP) has also been used for the extraction of triazine herbicides (65–69) and thiabendazole (70). The sol-gel prepared fibers are stable in strong organic solvents, as well as in acidic and basic solutions (25), depending on the precursor used. The sol-gel technology provides higher surface area for the fiber (39) due to its porous-like characteristics. A fiber coated with PDMS, a liquid coating polymer, is the most frequently used fiber for the extraction of nonpolar pesticide residues from fruit and vegetable samples (2, 14, 23, 28, 29, 38, 42, 43, 47, 51, 52, 71, 72). This is due to its rugged and robust nature and its ability to withstand high injector temperatures, between 280 and 320°C (6, 22); it also allows analysis of a wider linear range of concentrations (28). It is a nonpolar fiber that has been widely used to extract nonpolar analytes, but it can also be used for the extraction of polar analytes after extraction conditions, such as pH, salt addition, and temperature, are optimized. PA fiber is a solid crystalline coating that exhibits extraction capabilities inherent in a liquid coating absorption. It is suitable for the extraction of more polar pesticides (35, 45, 72–76) and has smaller diffusion coefficients compared to PDMS fiber coatings (22). The mixed phase coating fibers, such as PDMS/DVB, CW/DVB, CW/template resin (TPR), and CAR/PDMS, which are partially cross-linked, and DVB/CAR/PDMS (highly cross-linked), have properties that are complementary with their constituents (22) and have an increased retention capacity as a result of their mutually potentiating effect of adsorption (6), and higher distribution coefficients compared to PDMS and PA.

The mixed fiber coatings have also been widely used for the extraction of different classes of pesticide residues from fruit and vegetable samples. The PDMS/DVB fiber is the most widely used mixed-phase fiber coating. It has been used to extract pyrethroid pesticides from tomato and strawberry (7), polar fungicides from cherries, lemons, oranges, and peaches (36); 70 different pesticides from cucumbers, peppers, and tomatoes (50); and 56 pesticides from fruit juices (49). It has also been applied to phenylurea and carbamate pesticides from aqueous samples (56); water-soluble pesticides from tomatoes (51); carbendazim and thiabendazole pesticides from apples (77); six fungicides from tomatoes (78); carbamates and phenylureas from oranges, strawberries, cherries, and apples (79); four pesticides from grapes and apples (80); pyrethroid pesticides from cucumbers and watermelons (81); and four pesticides from strawberries (48). PDMS/DVB resulted in better extraction efficiency, good linearity range, lower LOD, good recovery, and better RSD compared to PDMS and PA. Other mixed fiber coatings that are available commercially (CAR/DVB, CW/TPR, CAR/PDMS, and DVB/CAR/PDMS) are rarely used for the extraction of pesticide residues from fruit and vegetable samples.

Optimization of Sample Matrix-Related Conditions

The extraction temperature affects the diffusion coefficients of the analytes in the sample and the distribution constants of the analytes between the sample and fiber. The diffusion

coefficient is connected with diffusion of analyte in the sample and the distribution constant with distribution of analyte between the sample and fiber. An increase in the extraction temperature enhances the transport of analyte from the sample matrix and leads to an increase in the extraction rate (6, 58) by increasing the diffusion coefficient. The partitioning of the analytes into the coated fiber is an exothermic process; hence, an increase in temperature causes a decrease in the distribution constant. This decreases the amount of analyte extracted at equilibrium, but the decreased amount may be acceptable if the target LOD can be reached. Therefore, an optimal and adequate extraction temperature, which depends on the sample matrix and the stationary phase used, is always used to provide satisfactory sensitivity and a high rate of extraction. A consistent fiber exposure time is also important for good accuracy and precision. Pesticides with low diffusion coefficients have a longer equilibration time (22), and a longer extraction time favors the extraction of higher amounts of analyte. Temperature and equilibrium time are closely related, because an increase in the extraction temperature decreases the distribution constant and shortens the equilibrium time due to less analyte being extracted at equilibrium.

Extraction efficiency can be improved by agitation (2, 30, 35, 36, 82), because it reduces the diffusion layer (7) and improves mass transfer from the sample matrix onto the fiber coating (75). Previous studies have shown that the rate of extraction increases with an increase in stirring, and thus, a decrease in the equilibrium time. Although there is a maximum sensitivity at the equilibrium time, full equilibration is not necessary because an accurate and precise analysis can be achieved before equilibrium is reached (33). At the same time, faster agitation tends to be uncontrollable and the rotational speed might cause a change in equilibrium time (29); a higher stirring rate can lead to magnetic flutter and air bubble formation in the solution (64), which can lead to poor precision and accuracy. There are different methods of agitation, i.e., magnetic stirring, fiber vibration, sonication, and flow-through cell extraction for the determination of pesticides, but studies have shown that there is no significant difference in the accuracy and precision of magnetic stirring, fiber vibration, and flow through cell agitation methods (82).

The addition of salt is also an important parameter. It has been found that saturating the sample matrix with salt helps to decrease the LOD by increasing the distribution constant (15). The partition coefficients depend on the matrix-analyte-fiber interactions (83). Since water-soluble pesticides have low affinity for the coated fiber, the extraction is increased by reducing their solubility via the addition of salt which changes their ionic strength (60). Recovery of water-soluble and polar analytes is improved by salt addition (75), but too much salt decreases the extraction efficiency because the sample matrix can be saturated and the undissolved salts may occupy active sites in solid coatings, thereby restraining partition between the analyte and the fiber (46). However when analyzing fruits and vegetables, it is important to add salt to normalize the random salt concentration in natural matrixes.

Sodium chloride has been widely used in SPME applications (2, 30, 35–37, 46, 49, 74–76), resulting in higher sensitivities in some cases, while potassium sulfate (39), sodium hydrogen sulfate (56), and other salts such as sodium hydrogen carbonate, potassium carbonate, and ammonium sulfate have also been

used (6) and were effective for the extraction of analytes onto the coated fiber due to their salting-out effects. The pH of the sample is also important in extraction techniques, and the nature of pesticides present in the sample depends on the pH of the sample matrix (6). Therefore, addition of acidic solution to the sample when analyzing acidic analytes and alkaline solution for basic analytes, increases extraction efficiency. The sample solution can be maintained at a desired pH by using a buffer solution.

Pesticide residues in fruit and vegetable samples cannot be extracted directly onto the coated fiber without blending or homogenizing, and this depends on the type of sample to be extracted. The coated fiber cannot be directly submerged in fruit and vegetable matrixes, and therefore there is need to homogenize fruits and vegetable samples before their extraction. Improved diffusion of the analytes from this complex matrix to the fiber can be achieved by addition of organic solvents before SPME (74). Addition of water (18) helps to improve extraction and protect the coated fiber (35). The problem of matrix effect in analysis of fruits and vegetables is solved by obtaining an aqueous extract from the sample (28) followed by SPME. This preparatory method has been used successfully for the extraction of pesticide residues by both HS-SPME (14, 38) and DI-SPME (35, 36, 62). In HS-SPME, the HS volume affects extraction efficiency and should be carefully minimized (84) to avoid splashing of the solution into the coated fiber. The vial size and sample volume (6), with little or no HS volume, are also critical in DI-SPME and should be kept constant for a particular analysis.

In the in-tube SPME, extraction efficiency depends on the polarity, length of the capillary coating, number and volume of draw/eject cycles, and sample pH (6, 31). The extraction time has a direct relationship with the length of the capillary column, while it is inversely proportional to the linear flow rate (31). The rate of extraction can also be increased with an increase in the coating fiber distribution constant, volume of sample phase, and thickness of the extracting phase, and with a decrease in the void volume of the capillary coating (31, 56). Increase in the flow rate in the capillary and the use of narrow-bore HPLC has also been shown to accelerate the extraction process (31). All these parameters must be optimized in order to achieve good accuracy and precision of the extraction process.

Desorption Conditions

Good optimization of the parameters involves a selection of desorption conditions. Desorption time and temperature, and the position and depth of the fiber coating in the GC injector, should be optimized in thermal desorption of analytes. The desorption step should be done in the shortest time possible; therefore, the desorption temperature (maintained within its maximum recommended operating value) should be higher than or equal to the boiling point of the least volatile analytes (6, 58), and the initial temperature of the GC column should be kept low or even cryofocused (cooled) to avoid peak broadening (6, 84) and ensure sharper peaks. Efficient thermal desorption of analytes also depends on the volatility of the analytes and the thickness of the fiber coating (6). To ensure a high linear flow rate, a narrow-bore insert is required (6, 31), which ensures the efficient removal of the desorbed analytes. A split/splitless injector should be operated in the splitless mode (6, 84), which

ensures an efficient and complete transfer of analytes. A small volume liner (78.5×6.5 mm od $\times$ 0.75 mm id) should be used to avoid tailing, which occurs when a large volume liner is used.

When the SPME device is coupled to LC, solvent desorption is used. This can be carried out in two different ways: dynamic desorption, in which the analytes are removed by a moving stream of mobile phase, used when the analytes are not strongly bonded to the fiber; and static desorption, in which the fiber is soaked in the mobile phase or other strong solvent for a specified time, used if the analytes are strongly bonded to the fiber (6, 25). In both cases, a minimum amount of solvent is needed. The temperature and the linear flow rate around the fiber determine the time for complete and efficient desorption of the analytes from the coated fiber, and they must be optimized for better recovery.

With in-tube SPME, there is no need for a special interface for desorption (6). A section of a coated GC capillary is placed between the needle of an LC autosampler and the injection valve, and the analytes extracted onto the coating are easily desorbed by using a small volume of solvent or mobile phase (31). Carryover of analytes is lower or eliminated in the in-tube SPME compared to the fiber SPME (6), because the solvent desorbs all analytes adsorbed on the coated fiber.

Calibration Methods

A calibration method is used to establish the relationship between the measured signal of an analytical instrument and known concentrations of the analytes. In order to determine the concentration of an unknown sample in a chromatographic measurement, the amount of the analyte is determined by the peak area and the calibration function. The sample amount as weighed out, along with dilution or concentration steps are taken into account in order to be able to give the concentration of analyte in the original sample (85). The use of a calibration curve for the analysis of pesticide residues in fruits and vegetables helps to solve the problems encountered in quantification. Traditional calibration methods, such as external standardization (calibration curve; 23, 30, 42, 43, 73), internal standardization (2, 14, 49, 50, 78), isotopic dilution (86), and standard addition (37, 39, 63, 75), are efficient for quantification in the laboratory analysis of pesticide residues in fruit and vegetable samples using the SPME technique. Other calibration methods, i.e., equilibrium, exhaustive, and diffusion-based calibrations (20, 57), have been suitably used for on-site air sampling.

External Standardization

External standardization involves the use of the substance to be determined in the preparation of several standard solutions at different concentration levels. A relationship between the peak responses and the target standard solutions is obtained by plotting the peak areas determined against the concentrations at the different calibration levels (85), and by analyzing the sample with the same extraction conditions as the target analyte (20). The concentration of the target analyte in the sample can then be calculated using the calibration curve equation with a correlation coefficient (r^2) greater than or equal to 0.99. This method has widely been used in SPME in which a blank sample matrix is prepared to avoid a matrix effect. It does not require

an extensive sample preparation, but there is a need to keep the sample compositions, sampling procedure, and chromatographic conditions constant (20, 57).

Internal Standardization

Internal standardization involves the addition of a substance to the calibration and sample solutions. The internal standard (IS) is used as a fixed reference material and kept constant in the solutions (20, 85). The compound used is different from the analyte and should be well-resolved in the chromatographic separation. The calibration curve is plotted by determining the ratio of peak area of the analyte to that of the IS for the calibration solutions that contain different concentrations of analyte with a fixed concentration of the IS (20, 57). The area ratios are then used for sample calibration against the analyte concentration. The use of an IS helps to compensate for volume errors, variations in functioning of the instrument, matrix effects, losses of analytes during sampling, and irreproducibility in operating parameters (20, 57, 85, 86). Isotopic dilution using isotopic-labeled or deuterated compounds provides the highest accuracy and precision for IS quantification (85), but the compounds are not available for all analytes (20).

Standard Addition

The use of the method of standard addition involves spiking the sample matrix with a known concentration of the target analyte containing an unknown concentration of the analyte in the mixture, which is then analyzed. A plot of the responses of target analyte at different concentration levels is developed (20, 57), and the original concentration in the unspiked sample is determined by extrapolating the plot to zero response. The method of standard addition requires extensive sample preparation, but helps to compensate for matrix effects when it is not possible to acquire matrix-matched blank samples.

Analysis of Pesticide Residues in Fruits and Vegetables

Since its introduction, an extensive amount of research work has been done on the use of SPME for the extraction and subsequent chromatographic analysis of all classes of pesticides in fruit and vegetable samples. This section focuses on the SPME modes (including the optimization of various parameters as discussed previously in this review), calibration methods, and chromatographic methods adopted by various workers for the extraction and subsequent analysis of different classes of pesticide residues in fruits and vegetables.

Nonpolar organochloride pesticide (OCP) (*o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD) and pyrethroid pesticide (PP) (fenpropathrin, beta-cyfluthrin, cyhalothrin, and bifenthrin) residues were determined in celery cabbage, garlic, and cabbage by Zeng et al. (64) using a 70 μ m polymethylphenylsiloxane-coated fiber prepared by a sol-gel process. The homemade fiber showed better extraction efficiency for the pesticides compared with the commercially available fibers (85 μ m PA, 100 μ m PDMS, and 65 μ m PDMS/DVB). This was attributed to its longer coating (1.5 cm), its porous nature, and the presence of a phenyl group that enhances π - π interaction between the fiber and the selected pesticides. The samples of cut-up vegetables (10 g) were mixed with 4 μ L of 10 μ g/mL standard solution

and dried for 30 min, followed by addition of 20 mL acetone; the mixture was mixed ultrasonically for 20 min. The extract was transferred into a 100 mL volumetric flask and diluted with 100 mL ultrapure water. A 10 mL aliquot of the solution was placed in a 15 mL glass vial and was extracted by DI-SPME at room temperature for 20 min, which showed higher extraction efficiency than the HS-SPME at 90°C for 30 min, stirred at 1000 rpm. The extracted analyte was desorbed at 280°C for 4 min into a GC-electron capture detector (ECD) instrument for analysis. A dilution factor was not considered due to the low solubility of the PPs in water. The extraction and desorption temperature and time, extraction mode, and fiber type were chosen after full optimization of the conditions. Addition of salt to the sample matrix decreased extraction efficiency and, thus, was not used in the method validation steps. Quantification was performed by external standardization in a blank vegetable spiked at 0.5–100 ng/g and analyzed in triplicate. The linear range was found between 0.5 and 100 ng/g for *p,p'*-DDE, *p,p'*-DDD, and bifenthrin, and from 2 to 100 ng/g for *o,p'*-DDT, *p,p'*-DDT, fenpropathrin, beta-cyfluthrin, and cyhalothrin with r^2 greater than 0.99 for all pesticides. The recovery of the pesticides spiked in various vegetables at 4 ng/g ranged from 42.9 to 105.3%, the RSDs ranged between 2.6 and 16.2%, and the LOD was between 0.13 and 1.45 ng/g.

Chai et al. (72) developed an HS-SPME-GC-ECD method for the multiresidue analysis of organophosphorus (OPP) (diazinon, malathion, chlorpyrifos, profenofos, and quinalphos) and OCP (α - and β -endosulfan and chlorothalonil) residues in tomatoes and guava. The developed method involved the extraction of 1 g of homogenized sample of fruits and vegetables in 100 μ L 20% methanol–acetone (1 + 1, v/v), and distilled water containing 10% NaCl was added to make a total mass of 5 g. The mixture was extracted with a 100 μ m PDMS fiber, which was selected due to its lower LOD and higher sensitivity for all pesticides investigated. The extraction was carried out in the HS mode under constant stirring (800 rpm) at 60°C for a pre-equilibrium time of 30 min, and desorbed at 240°C for 6 min after optimization of the necessary parameters. The IS (1-chloro-4-fluorobenzene), added to the sample mixture before SPME extraction, was used for quantification. The detection response of the fiber was enhanced by addition of water up to an optimum dilution factor, giving recovery between 82 and 97%, with RSD ranging from 0.3 to 3.3% ($n = 3$). The linearity ranged from 0.5 to 5000 μ g/L, and the LOD was between 0.1 and 1 μ g/L.

A method for the determination of seven PPs (bifenthrin, λ -cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, and τ -fluvalinate) in water, tomato, and strawberry samples was proposed by Beltran et al. (30). The method developed was based on DI-SPME and subsequent desorption into the injection port of a GC/MS system. The SPME procedure involved the extraction of 0.5 g of chopped samples of tomato and strawberry mixed with 2.5 mL distilled water and 3 mL 20% NaCl, and was thoroughly mixed by shaking in an ultrasonic bath for 30 min. Extraction parameters were optimized, and the maximum peak area was observed at an extraction temperature of 40°C, an equilibrium time of 30 min in 5 mL vials, and an agitation speed and time of 120 rpm and 20 s, respectively, using 65 μ m PDMS/DVB fiber. The fiber used showed efficient absorption of the pesticide residues and an increase in extraction efficiency using a mixture of hexane–acetone (1 + 1, v/v) as the extraction

solvent. The extracted pesticides were desorbed for 5 min into the GC instrument injection port with the mass spectrometer detector at 270°C (optimized time for complete desorption). The linearity, RSD, LOD, and LOQ values were determined by plotting a five point calibration curve (external standardization) prepared in matrix by spiking blank chopped tomato samples with a methanolic standard mixture of the PPs, and analysis was performed using the developed method by GC/MS in the selected ion monitoring (SIM) mode by selecting one target ion and two to four reference ions. The DI-SPME procedure showed a linear behavior in the range of 0.01 to 0.1 µg/L, with r^2 values ranging from 0.976 to 0.999. The LOD was between 0.003 and 0.025 mg/kg and LOQ for all pesticides investigated was 0.05 mg/kg with RSD ($n = 3$) determined at three different concentration levels. RSD was below 20% at 0.25 mg/kg and below 25% at 0.1 and 0.05 mg/kg.

Berrada et al. (35) investigated residues of three phenylurea pesticide (PUPs)—metobromuron, monolinuron, and linuron—and their aniline homologs in vegetable samples, including carrot, onion, and potato. A 50 g portion of a previously cut vegetable sample was extracted in a juice extractor, and the aqueous extract was made up to 50 mL with ultrapure water. A 5 mL aliquot was extracted in the presence of 14% (w/v) NaCl at pH 4 for analysis of PPs and pH 11 for both PP and aniline metabolites. The mixture was extracted using an 85 µm PA fiber at a room temperature for 60 min and desorbed at 300°C for 5 min, and extraction variables were optimized using GC with a nitrogen–phosphorous detector (NPD) and MS detector. The linearity ranged from 2.5 to 2500 µg/kg, with r^2 greater than 0.995 for both PUPs and their aniline metabolites. LOQ ranged from 0.1 to 2.2 µg/kg, and average recoveries of less than 10% were obtained for the herbicides analyzed, with the MS detector showing lower LOQ and recoveries compared to NPD.

A new fiber coating, vinyl crown ether prepared by the sol-gel process, was used by Cai et al. (37). The fiber had higher extraction efficiency and sensitivity for OPP pesticides (dichlorvos, phorate, diazinon, methyl parathion, fenithrothion, malathion, parathion, and ethion) compared to the commercial fibers 85 µm PA and 65 µm PDMS/DVB. The extraction efficiency was attributed to the cavity structure and strong electronegative effect of the heteroatoms on the ring of the crown ether, as well as its porous three-dimensional network, making it exhibit medium polarity, which provides a higher surface area and better selectivity for polar compounds. The extraction involved the optimization of several factors affecting the performance of SPME in fruit samples (apple, apple juice, and tomato). All extractions were performed in a 25 mL vial containing a 15 mL aliquot, obtained by fortifying a comminuted and homogenized fruit sample with an appropriate pesticide standard solution and diluting with water containing 5 g NaCl. The HS- and DI-SPME mode was used for 45 min at 70°C and 60 min at 30°C, respectively. The extracted analytes were desorbed for 5 min into a GC instrument with an MS detector at 270°C. HS-SPME showed good extraction efficiency and was selected for further method validation. The dilution of sample matrix with water, at a dilution ratio of 1:30, 1:50, and 1:70 for apple juice, apple, and tomato, respectively, reduced the matrix effect and improved recovery. The analytical method was validated using standard addition, and the LODs were 0.003–0.075 ng/g for apple juice, 0.032–0.09 ng/g for apple, and 0.0042–0.076 ng/g for tomato. The relative recovery

was between 55.3 and 106.4% for sample matrix spiked at three different concentration levels, with RSD between 3.3 and 10.1% ($n = 3$). The linearity range was 0.1–0.5 ng/g for apple and apple juice, and 0.1–100 ng/g for tomato, with r^2 greater than 0.993 in all samples analyzed.

Chai et al. (29) proposed an analytical procedure based on ultrasonic extraction of target analytes (carbaryl, diazinon, malathion, chlorpyrifos, profenofos, quinalphos, α - and β -endosulfan, and chlorothalonil) from cucumber and tomato. A 1.0 g portion of homogenized vegetable samples was diluted with 5 mL of distilled water followed by DI-SPME. The method involves immersing a 100 µm PDMS fiber into a solution of previously extracted sample at room temperature under magnetic stirring for 15 min. The extracted analytes were desorbed in the split mode into a GC-ECD instrument injector for 7 min at 270°C. Calibration curves were constructed by extraction of target analyte in aqueous solution spiked with standard solutions at seven different concentration levels and a constant volume of IS. All extraction conditions were optimized, and the optimum values were selected for method validation. The SPME procedure showed a linear behavior between 0.001 and 200 mg/kg, with r^2 values for all pesticides greater than 0.994. The LOQ ranged from 0.0005 to 0.01 mg/kg with LOQ between 0.001 and 0.05 mg/kg in water spiked with pesticides. Recoveries were between 53 and 75% for cucumber and 53 and 82% for tomato, with RSD ($n = 3$) below 10% (1.27–8.93% for cucumber and 0.47–9.3% for tomato).

Chai et al. (46) evaluated the use of CC-SPME combined with GC–NPD for the determination of five OPPs in tomato. The method involved simultaneous cooling of the fiber used in the HS mode and heating the sample matrix. The method developed showed a better extraction efficiency in terms of sensitivity, linearity, and recovery than the traditional HS-SPME. The procedure involved extraction of 5 g of spiked homogenized tomato sample, mixed with 10 mL water containing 2 g NaCl, at 80°C for 30 min using CC-HS-SPME with an activated carbon fiber, and desorption at 270°C for 2 min. The method was compared to the traditional HS-SPME based on the same parameters. The two methods showed acceptable linearity, recovery, and LODs. The CC-HS-SPME showed a wide linear range (1–200 ng/g), with r^2 better than 0.987, and low detection limits (0.2–0.5 ng/g). The mean recoveries ranged from 82.5 to 90% with RSD of 5.9–8.7% ($n = 3$), which was better than the results obtained by HS-SPME (lower than 9.2%).

An SPME-GC/MS method for the determination of eight OPPs (phorate, diazinon, methyl parathion, fenithrothion, malathion, fenthion, ethyl parathion, and methidathion) in different fruit juices and wine was developed by Zambonin et al. (76). The juice samples were centrifuged and diluted as required, while the wine sample was directly subjected to SPME without dilution. The DI-SPME extraction was carried out at room temperature under magnetic stirring for a nonequilibrium time of 30 min using an 85 µm PA fiber. The analytes adsorbed on the fiber were desorbed at 250°C for 5 min. Validation of the developed method was based on quantification with an external standard prepared by spiking the analytes in 10 mL of triple-distilled water. The calibration curves gave good linearity for all investigated ranges (10–500 µg/L) and r^2 better than 0.992. The estimated LOD and LOQ ranged from 2 to 90 and 7 to 297 µg/L, respectively, in all the fruits investigated. The addition of salt and dilution with water caused a significant difference in

extraction, while change in pH (4–11) had no significant effect on the extraction efficiency.

Blasco et al. (36) established an analytical procedure for the determination of postharvest, relatively polar fungicides, viz, dichloran, flutriafol, *o*-phenylphenol, prochloraz, tolclofos-methyl, in fruits (cherries, oranges, and peaches) using SPME-LC/ion trap-MS/MS with atmospheric pressure chemical ionization (APCI) and multiple reaction monitoring. The selectivity of LC/MS/MS was compared with LC/diode array detector (DAD) and LC/MS. One gram of sample was homogenized in acetone–water (5 + 1, v/v) by sonication for 15 min, then centrifuged at 3000 rpm for 20 min and filtered, and the filtrate was evaporated. The resulting aqueous solution was extracted by DI-SPME in a 2 mL vial, adjusted to 1 mL with water containing 300 mg NaCl, with continuous stirring (1000 rpm) for 90 min using a CW/TPR fiber coating. The extracted analytes were desorbed into an LC injection port operated in the static mode using methanol–water (70 + 30, v/v) for 10 min. The method validation showed good linearity and sensitivity, with LOQ (0.0005–0.01 mg/kg). The quantification determined using a six point calibration curve for fruit samples spiked with the analytes gave an LOD of 8 µg/L for dichloran; 80 µg/L for flutriafol, *o*-phenylphenol, and tolclofos-methyl; and 120 µg/L for prochloraz. The recoveries were between 8 and 69%, with prochloraz the lowest (5–22%), with RSD of 0.5–12% ($n = 3$) and linearity range of 0.0005 to 10 mg/L ($r^2 > 0.995$). Pesticide residues were detected in 60% of the fruits analyzed with tolclofos-methyl exceeding the maximum residue levels (MRLs). The extraction efficiency of CW/TPR, PA, PDMS/DVB, and PDMS (7, 30, and 100 µm) fibers was evaluated. The 100 µm PDMS gave the best recoveries, and the PDMS/DVB fiber exhibited slightly better extraction efficiencies for the analytes than CW/TPR. However, the CW/TPR fiber was used for the analysis because the PDMS/DVB coating was stripped off after two desorptions in the interface with a water–methanol mixture.

Chai et al. (38) developed HS-SPME-GC-ECD methods for the analysis of five OPPs (diazinon, malathion, chlorpyrifos, profenofos, and quinalphos) and three OCPs (α - and β -endosulfan, and chlorothalonil) in fruit (star fruit, strawberry, and guava) and vegetable (cucumber and tomato) samples. A 1 mL aliquot of the pesticide standard was spiked into 30 g of chopped fruit and vegetable sample dropwise, the mixture was kept at room temperature for 1 h, and 30 mL distilled water added. The resulting mixture was homogenized, and a 5 g aliquot was placed in a 15 mL clear glass vial and extracted using a 100 µm PDMS fiber in the HS mode. The extraction conditions (60°C, 30 min, stirring) were chosen after careful optimization of the variables. Complete desorption was achieved at 240°C for 15 min. Quantification was carried out with a five point calibration using an IS and the analytes spiked into the sample matrix, using a dilution factor of 2 and 2% (v/w) organic solvent. The recovery which was increased by the addition of water and organic solvent, had an average range of 70–99%, with RSD less than 10%, for all pesticides spiked into all the fruit and vegetable samples investigated. The calibration curve showed linearity between 1 and 400 mg/kg, with r^2 greater than 0.99.

Chai and Tan (14) performed the validation of the optimized HS-SPME parameters for the analysis of diazinon, malathion, chlorpyrifos, profenofos, quinalphos, α - and β -endosulfan, and

chlorothalonil in strawberry, guava, cucumber, tomato, and pakchoi using a previously developed method (72). Thermal desorption was carried out at 240°C for 10 min instead of 6 min used previously, which helped to overcome the carryover problem and the reduction in the gas chromatograph injector port temperature. The results showed that desorption for 10 min gave a better extraction efficiency than a 4 min desorption time. The average recovery obtained for each pesticide ranged from 71 to 98% at three fortification levels, with RSD less than 5% ($n = 3$). Repeatability (0.3–3.7%) and intermediate precision (0.8–2.5%) was satisfactory for all samples investigated. Quantification using an IS yielded an LOD of 0.01–1 µg/L and LOQ of 0.05–5 µg/L, with linearity between 0.1 and 5000 µg/L and r^2 greater than 0.99.

Chai and Tan (2) also developed an HS-SPME method to investigate the effects of washing fruit and vegetable samples with different solutions on the persistence of OPP and OCP residues. The extraction procedure followed a previously developed method (14) and the use of pesticide-free samples. The pesticide-free samples (strawberry and cucumber) were soaked for 1 h in tap water spiked with 2 mL of standard stock solution of different concentrations (0.5–50 mg/L). The spiked samples were air-dried at room temperature and soaked in acetic acid, sodium carbonate, sodium chloride, and water (5 and 10% each) for 10 and 30 min. The dried samples were extracted by HS-SPME at 60°C for 30 min with stirring at 800 rpm without pH adjustment and desorbed by GC-ECD at 240°C for 10 min. The method linearity ranged from 0.1 to 5000 µg/L ($r^2 > 0.996$), with RSD <4%. The LOD was 0.01 mg/L and LOQ was between 0.05 and 5 mg/L, which is three orders of magnitude lower than the European Union MRL (50–5000 mg/L). The results showed that washing with various solvents of different pH effectively reduced the residues of OPP and OCP on fruits and vegetables. Acetic acid was the most effective solvent, removing more than 70% of pesticide residues. The percentage removal increased with increase in concentration of the solvents and treatment time; the amount of pesticide residues removed by various solvents was also dependent on the solubility of the pesticides in water.

A vanguard-rearguard method was developed by Cortes-Aguado et al. (50) for the analysis of 70 multiclass pesticides (MCPs) from cucumber, pepper, and tomato. The method is based on binary analysis: the screening (vanguard) method is used to classify samples as negative or potentially non-negative (samples that contain pesticides higher than the MRLs), and a quantifying (rearguard) method is applied to samples that are previously classified as potentially non-negative. The extraction step involves the pre-extraction of the analytes with 10 mL of ethyl acetate using 4 g of the sample, followed by evaporation and redissolving of the residue in 10 mL water–acetone (9 + 1, v/v). The IS solution (5 µL) was added to a 1 mL vial and the volume filled up with the water/acetone extract, which was then extracted using a 65 µm PDMS/DVB fiber in DI-SPME mode at ambient temperature for 55 min. The extracted analytes were desorbed into a GC/MS instrument for 9 min at 250°C. Only 12 pesticides were confirmed, and the procedure gave good extraction efficiency, with recoveries between 77 and 106% and RSD of 3–11%. The LOD (0.0006–5 µg/kg) and LOQ (0.002–3 µg/kg) were one to three orders of magnitude below conventional pesticide residues methods. All samples

that were analyzed contained pesticide residues, but only the pepper sample was above the MRL.

Chen et al. (53) proposed a method based on FMAE, using 132 W microwave energy coupled to an SPME device. The microwave energy was used to irradiate the sample in a 50 mL ground glass-stoppered bottle containing 2 g of whole sample dissolved in 20 mL aqueous solution spiked with 300 µg/L dichlorvos in 10% ethylene glycol, and extraction was in the HS mode for 10 min at a pH = 5. The extracted analyte was desorbed into a GC-ECD instrument at 220°C for 3 min. The addition of salts to the sample solution decreased the extraction efficiency and was not used for method validation. The method was validated by plotting a calibration curve, which gave a linear range of 5–75 µg/L with an r^2 of 0.9985. Recoveries (106.1%) were good for all samples with RSD less than 8% (5.5–7.9%). The investigated pesticide (dichlorvos) was detected in pakchoi at a concentration of 8.65 µg/L.

A method was developed by Zambonin et al. (75) for rapid screening of triazole pesticides in wine and strawberry by optimizing the SPME-GC/MS conditions. A 50 g portion of homogenized strawberry sample was centrifuged for 30 s and mixed with 40 mL triple-distilled water and centrifuged again, while the wine sample was filtered through a 0.45 µm Millex-HV filter and diluted 1:2 with an aqueous solution containing 0.2 g/L NaCl. The resulting aqueous solution of the strawberry sample was recovered and brought to 100 mL with an aqueous solution containing 0.2 g/L NaCl solution. Aliquots of 5 mL of wine and strawberry solutions were transferred into a separate 7 mL clear vials for SPME extraction. The extraction of the sample was carried out at 50°C for a pre-equilibrium time of 45 min under magnetic stirring using the DI mode; desorption was at 250°C for 5 min. The method was validated, and quantification was achieved by the standard addition method. The RSD ranged between 2 and 11% ($n = 5$), and the LOD estimated at S/N of 3 ranged from 30 to 100 mg/kg. The dynamic range of the method using the SIM mode was linear over at least two concentration decades with the r^2 better than 0.999 and an intercept not significantly different from zero. All pesticides investigated were detectable except for propiconazole and appeared completely separated from interfering peaks.

Chen et al. (71) proposed a method in which four pesticide residues were extracted by DI-SPME using a 100 µm PDMS fiber from a biphasic water/plant tissue mixture and analyzed by GC with a flame photometric detector (FPD). In the extraction procedures, plant tissues were not separated from the aqueous solution before extraction, the pesticides were distributed between the aqueous phase and plant tissue, and the SPME fiber was in equilibrium with the analytes in the aqueous phase. Optimum extraction conditions used were room temperature, 90 min, agitation, and pH = 7. The water/plant tissue partition coefficient of the pesticides was also investigated in a series of samples containing 50 g of fresh vegetables and various amounts of deionized water which were mixed well. Aliquots (5 g) of the resulting pastes were placed into 10 mL vials and extracted at the optimum conditions, and desorption was at 270°C for 5 min. Validation of the method gave LOD between 9 and 75 ng/g, with recovery of about 25.5% and RSD between 1.5 and 19.8% ($n = 15$). All four OPPs investigated showed good linearity up to 100 mg/L. The experimental water/plant tissue partition coefficient of the pesticides correlated remarkably with their octanol–water partition coefficients.

A new sol-gel derived bisbenzo-16-crown-5 (B16C5) ether/hydroxyl-terminated silicone oil (HO-TSO) SPME coating coupled to GC-FPD was used for method development in the analysis of 10 OPP residues by Yu et al. (61). The sample of orange juice was diluted in water (1 + 50), saturated with NaCl placed in a 25 mL vial, and spiked with pesticide standard solutions, while 10 g of pakchoi was cut and homogenized with 100 mL water (1:50); a 23 mL aliquot of each mixture was used for DI-SPME. Extraction temperatures of 55 and 20°C for orange juice and pakchoi, respectively, were validated at 60 min under constant stirring for all samples, and desorption was at 270°C for 5 min. The analyses was quantified using an IS to construct a six point calibration curve. The linearity of the curves was between 1 and 500 ng/g, with r^2 values greater than 0.99. The LOD ranged from 0.003 to 1 ng/g with relative recovery of 76.8–101.2% and RSD between 2 and 9.2%. Pesticide residues were found in orange (2.1 ng/g of triazophos and 10.2 ng/g of fenitrothion) and pakchoi (6.8 ng/g).

Cortés-Aguado et al. (49) proposed a vanguard-rearguard analytical method for the SPME determination of 54 MCP residues in orange, peach, and pineapple juice samples. The method was very simple and fast because sample throughput is reduced by 50%) and minimized human errors. The procedure involved the pre-extraction of 1 mL homogenized samples with 1 mL ethyl acetate and centrifugation for 2 min. A 0.5 mL aliquot of the ethyl acetate extract was evaporated in a vial by a gentle stream of nitrogen, followed by addition of 1 mL water–acetone (9 + 1, v/v) containing 0.2 mg/L IS. The resulting mixture was extracted using a 65 µm PDMS/DVB fiber in the DI mode at room temperature, with desorption at 250°C for 9 min. Similar extraction conditions were used for screening (vanguard) and confirmation (rearguard) methods, except with an extraction time of 10 and 55 min, respectively. Validation of the confirmation/quantification (rearguard) method gave good recovery between 71 and 107% with RSD of 2–17%. The LOD and LOQ varied between 0.01 and 16.7 and 0.1 and 50 µg/L, respectively, and linearity was from 0.01 to 1 µg/L, with r^2 higher than 0.99 for all samples.

Dong et al. (39) analyzed radish for residues of 12 OCPs, using a sol-gel derived calix[4]arene/hydroxyl-terminated silicone oil (C[4]/HO-TSO)-coated SPME fiber. The extraction was carried out in the HS mode. Samples of 100 g of radish were comminuted and homogenized with 100 mL water; the 25 g homogenate was further diluted to 100 mL with water. All extractions were performed in a 12 mL amber vial containing a 10 µL aliquot of the standard solution, 4 mL of radish matrix solution, and 1.0 g K₂SO₄, and were carried out at 70°C for 30 min with constant stirring at 600 rpm. The extracted analyte was desorbed at 270°C for 2 min for analysis by GC-ECD. Method validation, which was determined by a calibration curve constructed using the method of standard addition, gave a linearity of 1–10 000 ng/L, with r^2 greater than 0.992. Recoveries for all the analytes was between 79.85 and 119.3% with RSD ($n = 5$) of 7.61–13.1%. The LOD ranged from 0.185 to 21.7 ng/L. The higher extraction efficiency of the fiber used, compared to 100 µm PDMS, was attributed to π - π and hydrophobic interactions of the sol-gel prepared fiber.

Wang et al. (48) studied the analysis of the carbamate pesticides (CPs) methiocarb, napropamide, fenoxycarb, and bupirimate in strawberry using SPME-LC-DAD with 60 µm PDMS/DVB. An aliquot of 125 µL of mixed standard solution at 0.01 g/L, 50 and

100 μL at 0.05 g/L, and 50, 100, and 200 μL at 0.25 g/L were added to 25 g of frozen strawberry, respectively. The sample was defrosted, blended, and transferred into a 50 mL tube; 20 mL of water was added and then centrifuged. The resultant supernatant was collected in a 50 mL volumetric flask, and another 20 mL of water was added and centrifuged again. The final volume of the extract was adjusted to the mark with water. An aliquot of 4 mL of the extracted solution was subjected to SPME for 45 min at room temperature with constant stirring at 1000 rpm. The extracted analytes were separated on a Pinnacle (Restek, Bellefonte, PA) ODS Amine column (250×4.6 mm id $\times$ 5 μm) in a static mode with an acetonitrile–water (55 + 45, v/v) mobile phase at a flow rate of 1 mL/min. The calibration curve showing linearity of 0.05–2 mg/kg and r^2 values greater than 0.99 was constructed for quantification using strawberry spiked with a standard solution of pesticides. A good repeatability with RSD between 2.92 and 9.25% and LOD of 10–50 $\mu\text{g/kg}$ were obtained. The good repeatability of this method was attributed to the characteristic detection precision of the UV DAD, and the observed performance showed that SPME-LC is a good complementary analytical tool to SPME-GC for pesticide residue analysis in food, especially for thermally labile or nonvolatile pesticides.

A sensitive and efficient SPME method for the determination of seven PPs, including fenpropathrin, α -cyhalothrin, deltamethrin, fenvalerate, permethrin, τ -fluvinate, and bifenthrin, in cucumber and watermelon samples using LC combined with postcolumn photochemically induced fluorimetry derivatization and fluorescence detection was developed and validated by Vazquez et al. (81). A 1 g amount of chopped, mixed, and homogenized sample (cucumber or watermelon) spiked with standard solutions of pesticide mixture was diluted with Milli-Q water (1:10, w/v) in a 10 mL volumetric flask containing 2.5 mL of acetonitrile solution and 0.7 mL 0.1 mol/dm $\text{K}_2\text{HPO}_4/\text{H}_3\text{PO}_4$ buffer (pH 3). An aliquot of 3 mL of this solution was used for DI-SPME with 60 μm PDMS/DVB at 65°C for 30 min with a stirring rate of 1100 rpm. The extracted analytes were desorbed into an HPLC column by an acetonitrile–water (80 + 20, v/v) mobile phase in a static mode, and simultaneous detection with a DAD was 283 and 330 nm. Quantification was determined statistically according to the EURACHEM standard; the LOQ obtained was between 1.3 and 5 $\mu\text{g/kg}$ and the LOD between 0.1 and 1.1 $\mu\text{g/kg}$. Recovery values calculated at two concentration levels ranged between 91 and 110% with RSD ($n = 6$) of 2–9.4% for both fruit samples. The calibration curves showed a good linear relationship that ranged between 0.0013 and 1.5 mg/kg ($r^2 \geq 0.996$).

Natangelo et al. (80) compared the precision of different detectors (MS and MS/MS) for SPME-GC analysis of four CP residues in apple and grape juices. Food samples were prepared by diluting 50 μL of liquid matrix, spiked at different concentration with the analytes in 10 mL distilled water containing 30% sodium chloride, placed in a 12 mL dark glass vial, and extracted in the DI mode at room temperature for 30 min with magnetic stirring. The extracted analytes were desorbed at 250°C for 15 min. A long desorption time was selected in order to purge any residue of the target analytes and to eliminate eventual interferences of co-extracted compounds. The precision of each detector was reported as the RSD of three replicates. The RSD values for the two detectors were comparable, but the MS detector gave a better precision (RSD

= 3.4–17.6%) than the MS/MS detector (RSD = 2.2–36.2%) for all analytes investigated in grape and apple juices, while the MS/MS detector yielded better precision for myclobutanil (2.2%) and acetochlor (3.1%) compared to the MS detector in the white wine sample. The detectors gave good linearity ranging from 20 to 2000 $\mu\text{g/L}$, and the LOD was lower for the MS detector (0.1–3 $\mu\text{g/L}$) than the MS/MS detector (2–17 $\mu\text{g/L}$). The sensitivities of both detectors were generally comparable, with the GC/MS having the better sensitivity.

Farajzadeh and Hatami (63) proposed an analytical method for the determination of OCP, OPP, and organonitrogen pesticide residues in grapefruit. Six SPME fiber coatings containing different percentages of activated charcoal (AC) and polyvinylchloride (PVC) were evaluated for their extraction efficiency. The fiber containing 70:30 AC/PVC had the highest efficiency and was used for method validation. The analytes were extracted in the DI-SPME mode at room temperature for 25 min in the presence of 0.5 g NaCl at a constant stirring rate of 900 rpm, and were desorbed for GC-FID at 200°C for 5 min. The method gave good linearity ranging from 25 to 5000 ng/L, and recovery between 42 and 63% (RSD = 5.8–9). The LODs were 8–40 ng/L. The use of NaCl at higher concentrations decreased the extraction recoveries because the NaCl crystals can occupy some of the active sites of the coated fiber. The proposed fiber showed high extraction capacity, good stability, and low cost of production.

A method was described by Simplicio and Boas (28) for the analysis of residues of OPPs in pears and fruit juice. Samples of 20 g of fruit and juice were spiked at different concentration levels with the pesticide stock solutions. The fortified juice was diluted (1:100) and extracted by DI-SPME using a 100 μm PDMS fiber for 25 min at room temperature and 1250 rpm, then desorption into a GC-FPD instrument was for 2 min at 250°C. Linearity determined using a calibration curve for quantification was between 0.250 and 25 $\mu\text{g/L}$, with r^2 values greater than 0.998. The recoveries were good for all pesticides and ranged from 75.9 to 102.6%, with RSD of 1.6–8.7% for triplicate analysis. LOD and LOQ ranged from 0.004 to 0.014 and 0.016 to 0.070 $\mu\text{g/L}$, respectively. The recoveries improved by diluting samples of the fortified juice, and the recoveries observed were four times higher than those from the undiluted samples. The origin of interference was identified by separately adding sodium dodecyl sulfate and pectin to a standard solution of pesticides. It was found that suspended and dissolved matter could interfere with the analysis by forming micelles that slow down the diffusion of analytes towards the fiber. The effect of pectin was reduced by addition of pectinase. The proposed method was applicable for the routine analysis of pesticide residues in fruit, and the dilution with water helped to reduce matrix effects.

Menezes Filho et al. (74) developed a new analytical method for simultaneous determination of 14 MCP residues in mango using SPME-GC/MS. The sample (3 g) was weighed into a 20 mL vial, fortified with 50 μL of the pesticide standard solution, and allowed to stand for 10 min, followed by the addition of 10 mL of (20 + 80, v/v) isopropyl alcohol–water containing 5% NaCl at pH 3. The resulting mixture was stirred at 1000 rpm, the upper layer transferred to a 10 mL volumetric flask, and the volume completed with the alcohol–water mixture. The resulting solution was then transferred to a sealed 10 mL HS vial for the DI-SPME with an 85 μm PA fiber at 50°C for 30

min, while stirring at 250 rpm. The fiber was placed in the gas chromatograph injector for desorption for 5 min at 280°C. The method developed was validated using external standardization calibration with nine concentrations (1–500 µg/L), each analyzed in triplicate. The average relative recoveries ($n = 3$) for the lowest concentration level ranged from 71.6 to 117.5%, with RSDs between 3.1 and 12.3%. The addition of small portions of binary solvent mixtures (water–ethanol, water–isopropyl alcohol, and water–acetonitrile at 80+20 (v/v)) was investigated in order to reduce the matrix effect. The mixture of water/isopropyl alcohol efficiently extracted nine pesticides with larger peak areas compared to three in pure water. LOD and LOQs ranged from 1.0 to 3.3 µg/kg and from 3.33 to 33.33 µg/kg, respectively. The method was selective and sensitive with good precision and mean recoveries. The residue levels were below the MRL values of the pesticides investigated.

Fytianos et al. (73) collected a total of 150 samples of 21 types of fruits sold in Greek markets and analyzed them for the presence of OPP residues. The fruit samples (5 g) were homogenized in 5 mL water with a blender, and 3 mL of the homogenate was transferred into an SPME vial containing 0.8 g NaCl. The sample was then spiked with methanolic solutions of OPPs (50 and 500 mg/L) and placed in an HS vial. The resulting solution was subjected to HS extraction using an 85 µm PA fiber for 20 min. The analytes were desorbed by inserting the fiber into the heated injector port of the gas chromatograph for 4 min at 230°C. The method linearity ranged from 1.2 to 667 µg/L, giving r^2 values of 0.998–0.999. The LODs and LOQs ranged from 0.03 to 3 and 0.12 to 10 µg/L, respectively. Recoveries were low (0.3 to 3.1%) with RSD between 2.5 and 8%. The effects of washing and peeling were also investigated, and the results showed that 18% of the pesticide residue can be removed by washing, while peeling was more effective, removing about 85% of the residues.

A method based on SPME and CE/MS was described by Rodriguez et al. (27) for the determination of acidic pesticides *o*-phenylphenol, ioxynil, haloxyfop, acifluorfen, and picloram in apple, orange, grape, and tomato samples using a CW/TPR fiber. A 200 g fruit sample was chopped, and a 5 g portion was homogenized with 0.5 mL 0.1 mol/dm NaOH and 5 mL acetone by sonication for 15 min. The resulting supernatant was filtered, and the acetone was evaporated at 50°C under a stream of nitrogen. The resulting aqueous phase was placed in a 2 mL vial containing 250 mg NaCl, and the pH was adjusted to 3. The extraction was carried out by DI at a constant stirring rate of 1000 rpm for 120 min. The extracted analytes were desorbed from the fiber by sonication for 15 min at a buffer temperature of 15°C with 100 µL methanol and 0.5 mL running buffer (ammonium formate–formic acid). The recovery of the analytes ranged from 7 to 94%, and RSD was between 3 and 13%. The method was linear between 0.02 and 500 mg/kg, with r^2 values ranging from 0.992 to 0.997, and the LOQs were from 0.02 to 5 mg/kg.

Sanusi et al. (52) developed an analytical method for the determination of PPs using FMAE followed by SPME. A 25 g sample of frozen strawberry was immersed in 50% acetonitrile in a 20 mL beaker, spiked with a known amount of the mixed standard solution, drop by drop, and kept overnight at room temperature. The mixture was introduced into a microwave heating tube and was irradiated at 30 W. The cooled solution was collected and decanted. A 9 mL aliquot

of the supernatant was transferred into a vial, and a 100 µm PDMS fiber was immersed for 30 min at room temperature under constant stirring. The fiber was introduced into a GC/MS instrument injector for desorption at 270°C for 2 min. Calibration curves, constructed from blank strawberry spiked at different concentrations with standard solutions, showed a linear range between 1 and 250 µg/kg, with r^2 values greater than 0.992 and RSD below 15%. The LODs and LOQs were lower than 14 and 40 µg/kg, respectively. The validated method was compared to other analyses done on the same sample by two certified trading laboratories, and the residues were of the same order of magnitude, which were far below the MRLs.

Guillet et al. (51) developed a method that involved the use of microwave energy for a fast and controlled pre-extraction of 25 MCP residues from tomato. The tomato sample matrix was prepared by spiking 200 g of frozen tomato with a known aliquot of mixed standard solution dropwise, and keeping it overnight at room temperature. The spiked tomatoes were introduced into a microwave heating tube with 240 mL acetonitrile–water (50 + 50, v/v) and put into a microwave oven. The mixture was irradiated for 5 min at 30 W. The sample temperature under the microwave effect should not exceed 65°C in order to minimize the possible degradation of thermally labile pesticides; potential vapor loss was prevented by using a condenser on the top of the extraction vessel. The solution was collected, cooled to room temperature, and centrifuged in a brown bottle. Two 9 mL aliquots were removed for SPME analysis. The fibers used were a 100 µm PDMS (for water-insoluble pesticides) and a 60 µm PDMS/DVB (for water-soluble pesticides), and the SPME was carried out at room temperature with a stirring rate of 500 rpm for 45 and 30 min for water-soluble and water-insoluble pesticides, respectively. The use of MAE was effective in suppressing the matrix effects. It also showed high performance in terms of linearity, which ranged from 0.1 to 5000 and 10 to 1000 µg/kg for water-soluble and water-insoluble pesticides, respectively, and good repeatability with RSDs of 2.2 to 15.7%. The LOD (0.01–7.62 µg/kg) and LOQ (0.20–25.4 µg/kg) for all pesticides investigated were much lower than the MRLs.

Fytianos et al. (23) screened 13 different vegetables for the presence of OPP residues (diazinon, methyl parathion, fenitrothion, malathion, and parathion) using HS-SPME coupled to GC-NPD. Fresh vegetable samples (5 g) were cut, diluted with water (1:1) and then homogenized in a high speed blender. A 3 mL aliquot of the homogenate was transferred with 0.8 g NaCl into a 9 mL HS vial that was capped and shaken thoroughly with a Vortex mixer. The sample mixture was preheated for 15 min, then subjected to SPME at 70°C for 20 min using a 100 µm PDMS fiber. Desorption was at 230°C for 4 min. The linearity of the method was determined by plotting a calibration curve, and the results showed linear regression in the concentration ranges 20–662, 25–662, 4–662, 13.3–662, and 2.31–662 ng/g for diazinon, methyl-parathion, fenitrothion, malathion, and parathion, respectively, with r^2 values between 0.998 and 0.999. The LOD was between 0.06 and 5 ng/g, while the LOQ ranged from 0.21 to 13.3 ng/g. The RSD values were between 2.2 and 7.6%, with low but satisfactory recovery of 0.3–3.1%. The fiber performance was not affected by the sample matrix, which prolonged fiber life time.

An analytical method was developed by Sagratini et al. (79) for the determination of residues of the CPs pirimicarb, benfuracarb, carbofuran, carbosulfan, and diethofencarb and the

PUPs monolinuron, diuron, and monuron in orange, strawberry, cherry, and apple juices using SPME coupled to LC/MS and LC/MS/MS. The sample was prepared by centrifuging 7 mL of fresh fruit juice for 15 min, followed by filtration of the supernatant. A 5 mL aliquot of the filtrate was diluted with water (1 + 1, v/v) in a 1.5 mL screw-cap vial containing 30% NaCl and was extracted with 50 μ m CW/TPR and 60 μ m PDMS/DVB fibers at 250°C for 90 min at a stirring rate of 1000 rpm. The extracted analytes were desorbed in the static mode for 5 min, with methanol–water (70 + 30, v/v) mobile phase at a flow rate of 0.5 mL/min. The recovery ranged from 25 to 80% with RSD between 1 and 17%. The LOQ was between 0.005 and 0.05 ng/g, while the LOD ranged from 0.001 to 0.005 ng/g.

Falqui-Cao et al. (26) presented the results obtained when FMAE was used prior to SPME for the analysis of CP residues in strawberry. The method does not involve blending and centrifuging of the strawberry sample before extraction. A whole frozen strawberry (25 g) was weighed into a beaker, spiked with a known amount of pesticide standard mixture, drop by drop, and kept at room temperature overnight. The mixture was then transferred to a microwave heating tube and heated for 7 min at 30 W. The mixture was cooled to room temperature, and the supernatant was decanted into a brown bottle. A 4 mL aliquot of the extract was transferred into a vial containing 50 mg powdered Na₂PO₄ and was subjected to DI-SPME using a 60 μ m PDMS/DVB fiber and stirring at 1000 rpm for 45 min. The analytes were desorbed into an LC-DAD instrument injection port with acetonitrile–water–methanol (30 + 50 + 20, v/v/v) at a flow rate of 1 mL/min with simultaneous detection at 205 and 240 nm. The r^2 values were higher than 0.99, and linearity ranged from 0.05 to 1 mg/kg. LOD and LOQ ranged from 0.013 to 0.022 and 0.044 to 0.074 mg/kg, respectively, and RSD values from 3 to 7.3%. The use of FMAE as a sample pretreatment step preceding SPME for pesticide analysis was more efficient than the blending and homogenizing methods.

Hu et al. (47) described an SPME method for the determination of 16 MCPs in strawberry. A sample of frozen strawberry was weighed (50 g) into a 150 mL beaker, spiked with different concentrations of pesticide standard mixture, and mixed. A 25 g portion of the mixture was diluted with 40 mL water in a Teflon tube and centrifuged for 5 min at 5200 rpm. The supernatant was collected into a 100 mL flask and was diluted with distilled water. A 4 mL aliquot of the solution was transferred into a 5 mL septum-capped vial and the SPME fiber (100 μ m PDMS) was introduced. Extraction by DI was then carried out with stirring at 800 rpm for 45 min at room temperature. The extracted analytes were desorbed into a GC/MS instrument injector at 270°C for 3 min. The r^2 values for eight of the investigated pesticides were higher than 0.99; six between 0.98 and 0.99, and the others were between 0.95 and 0.97. The RSDs for 13 pesticides were less than 13%, while the others were greater than 20%. The pesticides with higher RSD (up to 88.9%) were unstable and degraded within 7 days.

The analysis of seven MCPs in tomato was investigated by Ravalo-Perez et al. (78) using micellar electrokinetic chromatographic (MEKC) analysis. The reversed electrode polarity stacking mode (REPSM) and SPME were used as on-line and off-line preconcentration procedures, respectively. A 5 g sample of homogenized tomato was ultrasound-extracted with 5 mL acetone for 5 min, and the extracts were evaporated to dryness at 45°C. A 10 mL aliquot of the tomato sample (pH

adjusted to 9.5 by addition of 1 mol/dm NaOH) was reconstituted with 10 mL water containing 3 g NaCl. The resulting solution was placed in a 16 mL screw-cap vial and extracted in the DI mode with a 65 μ m PDMS/DVB fiber at ambient temperature for 143 min with continuous stirring at 900 rpm. The analytes were desorbed from the fiber with 1 mL methanol by stirring for 13 min at 1000 rpm. The extract obtained from the SPME procedure was evaporated to dryness in a rotary evaporator at 40°C and reconstituted with water–sodium tetraborate (1 + 3, v/w). The injection was carried out following the REPSM procedure for MEKC-DAD. The recovery of the analyte ranged from 94 to 102%, and the RSD was between 3 and 13%. The method validated using a matrix-matched calibration curve was linear between 0.5 and 2.5 mg/kg. LOD values were between 0.134 and 0.476 mg/kg, and the recoveries were independent of the spiked concentrations for the different samples assayed.

Lambropoulou and Albanis (42) investigated the applicability of HS-SPME for the determination of seven OPPs in strawberry and cherry juice using GC-FID and GC/MS for analysis. A 200 g portion of the whole fruits was sliced and homogenized for 30 s, then centrifuged and diluted with water (1 + 1, v/v). The resulting solution was spiked with appropriate amounts of the standard solution (0.5–50 μ g/L). A 5 mL aliquot was transferred into a 10 mL amber vial followed by addition of 0.75 g Na₂SO₄. The mixture was extracted with a 100 μ m PDMS fiber placed 1 cm in the HS of the sample, kept at 75°C, for 45 min and agitated at 960 rpm. After extraction, the fiber was inserted into the hot injector of the GC system at 240°C for 2 min. The method was linear for the concentrations studied, with r^2 values between 0.986 and 0.999. The recovery ranged from 82 to 105%, with RSDs between 5.2 and 18.7% and LODs from 0.0025 to 0.050 μ g/L. The responses of the two detectors were similar for all pesticides and samples analyzed.

Hu et al. (77) developed an analytical method for the determination of the CPs carbendazim and thiabendazole in apple based on SPME-LC. A sample of apple was blended and 25 g of the blended, apple was transferred into a Teflon tube followed by addition of 20 mL water. The tube was vortexed and centrifuged, the resultant supernatant was collected in a 50 mL volumetric flask, and 10 mL water added. The extraction procedure was repeated, and the final volume of the extract was diluted with water. A 4 mL aliquot of the extract was subjected to DI-SPME with a 65 μ m PDMS/DVB fiber for 35 min at room temperature and continuous stirring at 1100 rpm. The fiber content was desorbed into the hot injection port of an LC instrument with a fluorescence detector in static mode for 8 min, with methanol–water (50 + 50, v/v) mobile phase at a flow rate of 1.0 mL/min. The method was linear over the range 0.01–1 mg/kg, with LOD between 0.003 and 0.005 mg/kg, LOQ of 0.006–0.01 mg/kg, and r^2 of 0.9995 and 0.9998. The recoveries were between 91.5 and 96.1%, with RSD between 3.3 and 4.7%. The sample pH had no significant effect on the extraction efficiency of the analyzed pesticides.

Lambropoulou and Albanis (17) developed an HS-SPME method in combination with GC/MS for the extraction and analysis of OPP residues using a 100 μ m PDMS fiber. The sample preparation involved mixing 5 g of samples containing 15% (w/v) of Na₂SO₄ with a known amount of water in a vial and equilibration. The SPME fiber was then exposed to the HS of the sample in the vial for 45 min at 75°C and agitated at 960 rpm. After extraction, the fiber was inserted into the hot

Table 1. SPME-GC analysis of pesticide residues in fruits and vegetables^a

Pesticides class	Matrix	SPME mode	Fiber type	Ext. time, min	Ext. temp., °C	Stirring, rpm	Salt	pH	Des. time, min	Des. temp., °C	LOQ	LOD	Recovery, % (RSD, %)	Linearity	r ²	Det	Ref.
OCP and PP	Celery cabbage, garlic, and cabbage	DI	60 µm PMPS	40	40	1000	n.r.	n.r.	4	280	n.r.	0.13–1.45 ng/g	42.9–105.5 (2.6–16.2)	0.05–45 ng/g	>0.990	ECD	64
OCO and OPP	Tomato and guava	HS	100 µm PMPS	30	60	n.r.	NaCl (10%)	n.r.	6	240	n.r.	0.1–1 µg/L	81–97 (0.3–3.3)	0.05–5000 µg/L	n.r.	ECD	72
PP	Tomato and strawberry	DI	65 µm PDMS/DVB	30	40	120	NaCl (20%)	n.r.	5	270	3–25 µg/kg	50 µg/kg	n.r. (20–25)	10–100 µg/L	>0.990	ECD	30
PUP	Carrot, onion, and potato	DI	85 µm PA	60	20	n.r.	NaCl (14%)	4	5	300	0.8–2.2 µg/kg	n.r.	76–90 (4–8)	2.5–2500 µg/g	>0.995	NPD	35
OPP	Apple, tomato, and apple juice	HS	80 µm B15/C5	45	75	n.r.	NaCl (5 g)	n.r.	5	270	0.1–0.7 µg/kg	3–90 ng/kg	55.3–106.4 (3.3–10.1)	0.01–100 ng/g	>0.992	MS	37
OCP, OPP, and CP	Tomato and cucumber	DI	100 µm PDMS	15	25	n.r.	n.r.	n.r.	7	270	n.r.	1–10 ng/g	53–82 (0.47–9.2)	0.011–200 µg/g	>0.992	ECD	29
OPP	Tomato	CC-HS	ACF	30	80	500	NaCl (2 g)	n.r.	2	270	1–50 ng/g	0.2–0.5 ng/g	82.5–90 (5.9–8.7)	1–200 ng/g	>0.992	NPD	46
OPP	Orange, grape, and lemon juices	DI	85 µm PA	30	25	n.r.	NaCl (1 g)	n.r.	5	250	n.r.	2–90 µg/L	5–98 (4–12)	10–500 µg/L	>0.992	MS	76
OPP and OCP	Strawberry, guava, pakchoi tomato, and cucumber	HS	100 µm PDMS	30	60	800	NaCl (19%)	n.r.	10	240	7–297 µg/L	0.01–1 µg/L	77.3–93.3 (1.1–4)	0.1–5000 µg/L	>0.996	ECD	14
OPP	<i>C. coronarium</i> plant	DI	100 µm PDMS	90	25	n.r.	n.r.	7	5	250	0.05–5 µg/L	4.7–9 ng/g	2.4–25.66 (1.5–19.8)	n.r.	n.r.	FPD	71
OPP and OCP	Cucumber, star fruit, strawberry, and tomato	HS	100 µm PDMS	60	30	n.r.	n.r.	n.r.	15	240	n.r.	n.r.	70–99 (<10)	1–400 mg/kg	>0.990	ECD	38
70 MCP	Cucumber, pepper, and tomato	DI	65 µm PDMS/DVB	10	25	n.r.	n.r.	n.r.	9	250	n.r.	0.0006–5 ng/g	77–106 (3–11)	0.002–500 ng/g	>0.990	MS	50
OPP	Strawberry, tomato, and pakchoi	MAE-HS		10	132 W	n.r.	n.r.	5	3	220	0.002–3 ng/g	1.0 µg/L	106 (5.5–7.9)	5–75 µg/L	0.9985	ECD	53
Triazole	Strawberry	DI	85 µm PDMS	45	50	n.r.	NaCl (1 g)	n.r.	5	250	n.r.	30–100 ng/kg	n.r. (2–11)	n.r.	0.999	MS	75
OPP	Orange juice and pakchoi	DI	B16/C5	65	20–50	n.r.	NaCl ([?])	n.r.	5	270	n.r.	0.003–1 ng/g	76.8–101.2 (2.3–9.2)	1–500 ng/g	>0.990	FPD	61
54 MCP	Orange and peach	DI	HO-TSO	55	25	n.r.	NaCl (5%)	n.r.	9	250	0.1–50 µg/L	0.01–16.7 µg/L	72–107 (2–17)	0.01–1 µg/L	>0.990	MS ²	49
OCP	Radish	HS	65 µm PA	30	70	600	K ₂ SO ₄ (1 g)	n.r.	2	270	n.r.	0.185–21.71 ng/g	75.9–119.3 (7.61–13.1)	0.0185–21.71 ng/g	>0.992	ECD	39

Pesticides class	Matrix	SPME mode	Fiber type	Ext. time, min	Ext. temp., °C	Stirring, rpm	Salt	pH	Des. time, min	Des. temp., °C	LOQ	LOD	Recovery, % (RSD, %)	Linearity	r ²	Det	Ref.
CP	Apple and grape juice	DI	60 µm C14/HS-TSO	30	25	n.r	NaCl (30%)	n.r	15	250	n.r	0.1–10 µg/L	n.r (2.2–36.2)	20–2000 µg/L	>0.996	MS	80
OCF, OPP, and ONP	Grape	DI	65 µm CW-DVB	15	25	900	NaCl (0.5 g)	n.r	5	200	n.r	8–40 ng/L	42–63 (5.8–9)	25–5000 ng/L	>0.990	FID	63
OPP	Pear and apple	DI	AC/PVC	20	25	1250	n.r	n.r	2	250	16–17 ng/L	4–14 ng/L	5.9–102.6 (1.6–8.7)	0.250–25 µg/L	>0.998	FPD	28
14 MCP	Mango	DI	100 µm PDMS	30	50	250	NaCl (5%)	3	5	280	3.3–33.3 ng/g	1–3 ng/g	71.6–117.5 (3.1–12.3)	3.33–1665 ng/g	>0.990	MS	74
OPP	21 fruits	HS	85 µm PA	20	n.r	n.r	NaCl (0.8 g)	n.r	4	230	0.12–10 µg/L	0.03–3 µg/L	0.31–3.1 (2.5–3)	1.2–667 ng/g	>0.998	NPD	73
PP	Strawberry	MAE-DI	85 µm PA	30	30 W	n.r	n.r	n.r	2	270	0.9–13.8 ng/g	2.84–41.3 ng/g	n.r (1.2–14.2)	1.0–250 ng/g	>0.998	MS	52
25 MCP	Tomato	DI	100 µm PDMS	45	25	500	n.r	n.r	2	250	0.20–25.4 ng/g	0.01–7.62 ng/g	n.r (2.2–5.7)	0.10–500 ng/g	>0.990	MS	51
25 MCP	Tomato	DI	60 µm PDMS/DVB	45	25	500	n.r	n.r	2	250	0.20–25.4 ng/g	0.01–7.62 ng/g	n.r (2.2–5.7)	10–1000 ng/g	>0.990	MS	51
OPP	Strawberry and cherry juices	HS	100 µm PDMS	45	75	960	Na ₂ PO ₄ (15%)	3.5	2	240	n.r	5–25 ng/g	82–100 (5.2–18.7)	0.5–50 µg/L	>0.986	MS	42
16 MCP	Strawberry	DI	100 µm PDMS	45	25	800	n.r	n.r	3	270	1–5 ng/g	n.r	n.r (3.8–88.9)	4–500 ng/g	>0.980	MS	47
OPP	Strawberry and cherry	HS	100 µm PDMS	45	75	960	Na ₂ PO ₄ (15%)	3.5	5	240	17–35 ng/g	6.3–12.7 ng/g	74–94 (7.8–14.6)	50–500 ng/g	>0.996	MS	43
OPP	13 vegetables	HS	100 µm PDMS	20	70	n.r	NaCl (.8 g)	n.r	4	230	0.2–13.3 ng/g	0.06–5 ng/g	0.3–3.1 (2.2–7.6)	2.31–662 ng/g	>0.998	NPD	23
SF	Grape, ketchup, strawberry, and tomato	HS	100 µm PDMS	25	100	500	NaCl (0.36 g)	7	5	250	5.5–9.4 ng/g	1.8–3.1 ng/g	90.4–106.4 (7.8–14.6)	12.5–250 ng/g	>0.998	MS	45
OPP	Strawberry, green apple, and grape	HS	80 µm PA	10	75	120	NaCl (1.5%)	n.r	5	250	15.1–16.2 ng/g	4.5–4.8 ng/g	65–125 (0.3–7.4)	0.005–0.7 ng/g	>0.999	ECD	88
TH	Onion	DI	PDMS/20H-Met18C6	25	40	500	NaCl (8%)	7	1	250	n.r	20–90 ng/L	90–96.4 (5.25–9.58)	0.05–9 ng/L	>0.992	GC/MS	66
TH	Onion	DI	MIP	20	40	500	NaCl (6%)	7	1	250	n.r	14–95 ng/L	85.2–95.2 (5.6–10.88)	0.05–10 ng/L	>0.992	GC/MS	67
TH	Onion	DI	MIP SA/MPI	12	n.r	600	NaCl (6%)	7	1	250	n.r	9–85 ng/L	86.1–97 (3.2–7.4)	0.02–16 ng/L	>0.992	GC/MS	68

^a n.r = Not reported; Ext. time = extraction time; Ext Temp. = extraction temperature; Des. time = desorption time; Des. Temp. = desorption temperature; Des. mode = desorption mode; Det. = detector; Ref. = reference; r² = correlation coefficients; other abbreviations are the same as used in the text.

injector of the GC system in the splitless mode at 240°C for 5 min. The results obtained gave a higher response by addition of water and solvent. Quantification was performed by constructing a calibration curve for the samples spiked with the analytes, and it showed linear response from 50 to 500 µg/kg with $r^2 > 0.986$. LODs ranged from 6.32 to 12.7 µg/kg, and LOQs between 17 and 35.7 µg/kg. The recoveries were between 74 and 94%, and RSD ranged from 7.8 to 14.6%. The developed method was in good agreement with results obtained by other methods, and had better efficiency in terms of time and accuracy.

Navalon et al. (45) analyzed grape, strawberry, tomato, and ketchup samples for residues of the strobilurin fungicides pyrimethanil and kresoxim-methyl using HS-SPME coupled to GC/MS. Samples were prepared by blending and spiking of the fruits with an appropriate standard in methanol and agitating for 60 min. The homogenates were then diluted with a buffer solution to adjust the pH to 7. An aliquot of 6 g of the diluted sample was transferred into a 14 mL vial followed by addition of NaCl and agitation. The mixture was extracted with an 85 µm PA fiber at 100°C for 25 min with stirring at 500 rpm. Desorption was carried out at 250°C for 5 min. Quantification of the analyte concentrations in the fruit samples was carried out by standard addition to avoid any matrix effect. The results gave good linearity ranging from 12.50 to 250 ng/g, with r^2 greater than 0.998. The recovery values were 90.4–106.4 and 7.4–15%, respectively. The LODs ranged from 1.8 to 3.1 ng/g, while the LOQs were between 5.5 and 9.4 ng/g. The extraction temperature (100°C) of the developed method is most suitable for stable pesticides, as many pesticides undergo hydrolysis at this temperature.

Degradation of the pesticides methyl-parathion, parathion, diazinon, and cypermethrin by dissolved ozone was investigated by Wu et al. (87). The effectiveness of pesticide oxidation in aqueous solution using a low level of dissolved ozone was determined using SPME-GC/MS. The homogenized slurry sample was extracted twice with acetone followed by cleanup with dichloromethane for the OPPs and petroleum ether for cypermethrin. It was then evaporated and reconstituted in acetone before DI-SPME at 15 and 30 min extraction time and subsequent analysis with GC/MS at a desorption temperature and time of 250°C for 3 min and 270°C for 5 min for the OPPs and cypermethrin, respectively. Dissolved ozone (1.4 mg/L) was effective in oxidizing 60–99% of methyl parathion, cypermethrin, parathion, and diazinon in aqueous solution in 30 min, and the degradation was mostly completed in the first 5 min. The removal efficiency of pesticides highly depended on the dissolved ozone levels and temperature.

Wan Ibrahim et al. (88) developed a new sol-gel hybrid coating, PDMS-2-hydroxymethyl-18-crown-6 in-house for use in SPME. The three compositions produced were assessed for their extraction efficiency towards three selected OPP residues (diazinon, chlorpyrifos, and profenofos) in strawberry, green apple, and grape samples. All three compositions of the sol-gel fiber showed superior extraction efficiencies compared to commercial 100 µm PDMS fibers. The composition showing the best extraction performance was used to obtain the optimized SPME conditions: 75°C extraction temperature; 10 min extraction time; 120 rpm stirring rate; 5 min desorption time; 250°C desorption temperature; and 1.5% (w/v) of NaCl addition. The method LODs ($S/N = 3$) of the OPPs with the new sol-gel hybrid material ranged from 4.5 to 4.8 ng/g. Recovery

of the new hybrid sol-gel SPME material ranged from 65 to 125% with good precision of the method (RSD), ranging from 0.3 to 7.4%.

The efficiency of MIP fibers for the SPME extraction of triazine herbicides (THs) has also been evaluated. Hu et al. (65) developed a novel MIP SPME fiber coupled directly to HPLC for the determination of the triazines prometryn, atrazine, simetryn, terbutylazin, ametryn, propazine, and terbutryn in complicated samples such as soy bean, corn, and lettuce. The dry samples were ground and sieved with a mesh gauge. Five grams of the ground samples were spiked with 5 µL 1 mg/L triazine mixed standard solution, and the extraction was performed in 3 mL solvent with a microwave oven at 60°C for 30 min. The microwave-extracted solutions were concentrated to remove the solvent and then dissolved in 10 mL of benzene. The resulting solutions (3 mL) were placed in a 5 mL glass vial and were extracted with the MIP-coated fiber in the DI mode for 30 min at a stirring rate of 1000 rpm. The extracted solution was desorbed for HPLC-UV analysis by acetonitrile–water (50+50, v/v) mobile phase for 10 min. A detector wavelength of 225 nm was used. The extraction yield of six TH analogs with the MIP-coated fibers was much higher than that of a nonimprinted polymer, which was attributed to the presence of hydrogen bonding interaction between secondary amino groups in the THs and the carboxylic groups in the MIP coating. The developed method yielded a good linear range of 0.1–2 µg/L with r^2 values of 0.9936–0.9994. LODs for the five THs were in the range of 0.012 to 0.090 µg/L, and recoveries ranged between 75.5 and 113.4% with RSD from 5.7 to 10.6%.

A monolithic SPME fiber was prepared based on atrazine-MIP for the determination of THs, such as atrazine, simazine, propazine cyanazine, prometryn, terbutryn, and 1,3,5-triazine, from onion and rice samples by Djozan and Ebrahimi (66). A weighed sample of onion was crushed with a juicer to produce juice and scum, and the liquid juice was spiked with two different amounts of the mixed THs to give final concentrations of 100 and 500 µg/L. The spiked sample was then stirred in an ultrasonic bath for 10 min and centrifuged, and 3 mL of the supernatant solution, with pH adjusted to 7 by addition of phosphate buffer, was transferred into a 4 mL vial containing 8% NaCl. The solution was extracted in the DI mode by an MIP fiber at room temperature for 25 min stirred at 500 rpm, and analytes were desorbed into a GC/MS instrument at 250°C for 1 min. The MIP polymer was shown to be thermally and chemically stable, and its extraction efficiency increased with increase in the pH of the sample solution. The analytical performance yielded LODs in the range of 20–90 µg/L, with average recoveries between 90 to 96.4% and RSD of 5.25–9.58% for the onion sample. The linear range was between 50 and 9000 ng/mL, with r^2 greater than 0.9925.

An ametryn-MIP fiber coated on a homemade glass capillary and an ametryn-MIP fiber coated on an anodized aluminum wire were prepared by Djozan et al. (67, 68) for the SPME extraction of the THs ametryn, prometryn, terbutryn atrazine, simazine, propazine, cyanazine, and 1,3,5-triazine from maize, onion, and rice samples. The sample preparation, extraction, and desorption conditions were the same as discussed in the earlier paper (66), but with 6% NaCl and extraction times of 25 and 12 min for the MIP fiber coated on a homemade glass capillary and ametryn-MIP coated on an anodized aluminum wire, respectively. The ametryn-MIP coated on an anodized

Table 2. SPME-LC analysis of pesticide residues in fruits and vegetables^a

Pesticides class	Matrix	SPME mode	Fiber type	Ext. time, min	Ext. temp., °C	Stirring, rpm	Salt	pH	Des. time, min	Des. mode	Solvent, v/v	Flow rate, mL/min	LOQ	LOD	Recovery, % (RSD, %)	Linearity	r ²	Det.	λ, nm	Ref.
Fungicides	Cherry, orange, and peach	DI	50 μm CW/TPR	90	n.r	1000	NaCl (30%)	n.r	10	S	MeOH-H ₂ O (70 + 30, v/v)	0.6	8–120 μg/L	0.05–100 μg/L	8–69 (8–12)	0.05–10 μg/g	>0.992	MS ²	210	36
CP	Strawberry	DI	60 μm PDMS/DVB	45	25	1000	n.r	n.r	1	S	MeCN-H ₂ O (55 + 45, v/v)	1	10–150 ng/g	n.r	n.r (2.92–9.24)	0.05–2 μg/g	>0.993	DAD	205/240	48
PP	Cucumber and watermelon	DI	60 μm PDMS/DVB	30	65	1100	n.r	3	5	S	MeCN-H ₂ O (80 + 20, v/v)	1	0.1–1.1 ng/g	0.3–5 ng/g	91–110 (2–9.4)	3–1500 ng/g	>0.996	PIF/FD	283/330	81
AP	Apple, grape, orange, and tomato	DI	50 μm CW/TPR	120	n.r	1000	NaCl (0.25 g)	2	n.r	n.r	n.r	7	n.r	0.02–5 μg/g	7–94 (3–13)	0.02–500 μg/g	>0.992	CE/MS	200	27
CP	Strawberry	DI	MAE/60 μm PDMS/DVB	45	30W	1000	NaCl (50 mg)	6	n.r	n.r	MeCN-H ₂ O-MeOH (30 + 50 + 20, v/v/v)	1	13–22 ng/g	44–714 ng/g	n.r (3–7.3)	51–500 ng/g	>0.990	DAD	205/204	26
CP	Apple	DI	60 μm PDMS/DVB	35	25	1100	n.r	n.r	8	S	MeCN-H ₂ O (50 + 50, v/v)	1	3–5 ng/g	6–10 ng/g	91.5–96.1 (3.3–4.7)	0.1–1 ng/g	>0.990	FD	315	77
TF	Orange juice	DI	MIP	60	n.r	600	NaCl (0.12 mol/dm)	10	30	n.r	MeCN-H ₂ O (70 + 30, v/v)	0.6	n.r	4 μg/L	6.9 and 7.0 (7.6 and 6.6)	0.1–5 mg/L	>0.995	FD	305/345	70
TBZ	Lettuce	DI	MIP	30	60	1000	n.r	n.r	10	n.r	MeCN-H ₂ O (50 + 50, v/v)	1	n.r	12–90 mg/L	75.5–113.4 (5.7–10.6)	0.1–2 μg/L	>0.993	UV	225	65

^a n.r = Not reported; Ext. time = extraction time; Ext. temp = extraction temperature; Des. time = desorption time; Des. temp. = desorption temperature; Des. mode = desorption mode; Det. = detector; Ref. = reference; r² = correlation coefficients; other abbreviations are the same as used in the text.

aluminum wire was had a higher efficiency compared to the MIP fiber coated on a homemade glass capillary, while the latter was better than PA and PDMS fibers. The LOD values were in the range of 14–95 and 9–85 µg/L, with average recoveries of 85.2–95.2% (RSD = 5.6–10.8%) and 86.1–97.0% (RSD = 3.2–7.4%). The calibration curves were linear in the range of 50–10 000 and 20–16 000 µg/L for the MIP fiber coated on the homemade glass capillary and ametryn-MIP fiber coated on an anodized aluminum wire, respectively. The r^2 was greater than 0.9925 for both fibers. The binding properties of the MIP fiber were also studied (67), and the experimental data fit well to the bi-Langmuir isotherm, showing the existence of two types of binding sites on the prepared fiber.

In a study by Barahona et al. (70) MIP monoliths coated on fused silica were prepared and evaluated for their use in supported liquid membrane-protected MIP-SPME of thiabendazole from orange juice. A volume of 1.7 mL of standard solution was added into a 2 mL vial and was extracted by the homemade MIP fiber in the DI mode for 60 min with stirring at 600 rpm. After the extraction, the fiber was washed in toluene to remove nonspecific interactions and then air-dried for 5 min. The extracted analyte was desorbed with methanol–acetic acid (95 + 5, v/v) by agitation at 600 rpm for 30 min in a 0.4 mL vial insert. The resulting acidic extract was then diluted (1:4) with methanol–water (70 + 30, v/v), which was also used as the mobile phase and injected for HPLC with simultaneous fluorescence (λ = 305 nm excitation and 345 nm emission) and UV (λ = 290 nm) detection. The calibration curves showed good linearity in the range of 0.01–5 mg/L with r^2 greater than 0.995. The LOD was 4 µg/L, and low recovery (6.9 and 7.0%) with RSD of 7.6 and 6.6% for low and high spiking levels, respectively, was obtained. Its limitation is the lack of selective recognition of the target analyte in aqueous solution (70), and the lack of compatibility between the solvent required to desorb the analyte from the MIP and the mobile phase used (69). However, its use as an SPME fiber has helped to improve the results of the analytical methodology in the extraction of THs and thiabendazole.

Conclusions

The need for frequent monitoring of pesticide residues and other contaminants in food commodities has led to the development of various sample preparation techniques. The SPME technique proved to be efficient, fast, and accurate for qualitative and quantitative analyses of pesticide residues in fruits and vegetables, and has continued to attract the attention of various stakeholders in the agricultural and food industries.

This review has attempted to summarize the various SPME modes, analytical procedures, and calibration methods used for the estimation of pesticide residues in fruits and vegetables. As observed, fiber coatings of different polarity and thickness were used for the extraction of different classes of pesticides. Most analysts selected the 100 µm PDMS fiber and used it in the DI mode, after an optimized dilution of the sample matrix. MIP fibers have also been effectively used for the extraction of strongly polar atrazine herbicide. The introduction of the sol-gel derived fiber that involved the covalent bonding of a polymer phase to a fused-silica substrate has helped to solve problems encountered in the use of commercially available fibers. The problems include low recommended operating temperature,

swelling of the fiber in organic solvents and water, breakage, and stripping of the coatings. The coupling of SMPE to GC which desorbs the analytes thermally, is the most widely used analytical approach for pesticide residues, but SPME has also been recently coupled to LC with mobile phase desorption and use of various detectors. Mass spectrometric detection is widely used for GC, while the DAD is applied for LC detection.

OPPs are among the most commonly applied pesticides in agriculture throughout the world. This is attributed to their ability to degrade more readily in the environment compared to other more persistent pesticides. This explains why a vast majority of the methods developed have been for OPP determination.

Summaries of SPME-GC and SPME-LC analyses of pesticides in fruits and vegetables are presented in Tables 1 and 2.

References

- (1) Sharma, D., Nagpal, A., Pajade, Y.B., & Katnoria, J.K. (2010) *Talanta* **82**, 1077–1089. <http://dx.doi.org/10.1016/j.talanta.2010.06.043>
- (2) Chai, M.K., & Tan, G.H. (2010) *Food Chem.* **123**, 760–764. <http://dx.doi.org/10.1016/j.foodchem.2010.05.038>
- (3) Bidari, A., Ganjali, M.R., Norouzi, P., Hosseini, M.R.M., & Assadi, Y. (2011) *Food Chem.* **126**, 1840–1844. <http://dx.doi.org/10.1016/j.foodchem.2010.11.142>
- (4) Araoud, M., Douki, W., Rhim, A., Najjar, M.F., & Gazzah, N. (2007) *J. Environ. Sci. Health A* **42**, 179–187
- (5) Pawliszyn, J., Pawliszyn, B., & Pawliszyn, M. (1997) *The Chemical Educator* **2**, 1–7. <http://www.springerlink.com/content/h72xx3624g122085>
- (6) Kataoka, H., Lord, H.L., & Pawliszyn, J. (2000) *J. Chromatogr. A* **880**, 35–62. [http://dx.doi.org/10.1016/S0021-9673\(00\)00309-5](http://dx.doi.org/10.1016/S0021-9673(00)00309-5)
- (7) Beltran, J., Lopez, F.J., & Hernandez, F. (2000) *J. Chromatogr. A* **885**, 389–404. [http://dx.doi.org/10.1016/S0021-9673\(00\)00142-4](http://dx.doi.org/10.1016/S0021-9673(00)00142-4)
- (8) Ahmed, F.E. (2001) *Trends Anal. Chem.* **20**, 649–661. [http://dx.doi.org/10.1016/S0165-9936\(01\)00121-2](http://dx.doi.org/10.1016/S0165-9936(01)00121-2)
- (9) Otero, R.R., Grande, B.C., & Gandara, J.S. (2003) *J. Chromatogr. A* **992**, 121–131. [http://dx.doi.org/10.1016/S0021-9673\(03\)00317-0](http://dx.doi.org/10.1016/S0021-9673(03)00317-0)
- (10) Štajnbaher, D., & Zupancic-Kralj, L. (2003) *J. Chromatogr. A* **1015**, 185–198. [http://dx.doi.org/10.1016/S0021-9673\(03\)01211-1](http://dx.doi.org/10.1016/S0021-9673(03)01211-1)
- (11) Alberio, B., Sánchez-Brunete, C., & Tadeo, J.L. (2003) *J. Agric. Food Chem.* **51**, 6915–6921. <http://dx.doi.org/10.1021/jf030414m>
- (12) Adou, K., Bontoyan, W.R., & Sweeney, P.J. (2001) *J. Agric. Food Chem.* **49**, 4153–4160. <http://dx.doi.org/10.1021/jf001528q>
- (13) Arthur, C.L., & Pawliszyn, J. (1990) *Anal. Chem.* **62**, 2145–2148. <http://dx.doi.org/10.1021/ac00218a019>
- (14) Chai, M.K., & Tan, G.H. (2009) *Food Chem.* **117**, 561–567. <http://dx.doi.org/10.1016/j.foodchem.2009.04.034>
- (15) Arthur, C.L., Killam, L.M., Buchholz, K.D., Pawliszyn, J., & Berg, J.R. (1992) *Anal. Chem.* **64**, 1960–1966. <http://dx.doi.org/10.1021/ac00041a034>
- (16) Kataoka, H. (2002) *Anal. Bioanal. Chem.* **373**, 31–45. <http://dx.doi.org/10.1007/s00216-002-1269-z>
- (17) Lambropoulou, D.A., & Albanis, T.A. (2007) *Anal. Bioanal. Chem.* **389**, 1663–1683. <http://dx.doi.org/10.1007/s00216-007-1348-2>
- (18) Pawliszyn, J. (1997) *Solid Phase Microextraction: Theory and Practice*, VCH, New York, NY
- (19) Zeng, E.Y., & Noblet, J.A. (2002) *Environ. Sci. Technol.* **36**, 3385–3392. <http://dx.doi.org/10.1021/es025653p>

- (20) Ouyang, G., & Pawliszyn, J. (2008) *Anal. Chim. Acta* **627**, 184–197. <http://dx.doi.org/10.1016/j.aca.2008.08.015>
- (21) Risticvic, S., Niri, V.H., Vuckovic, D., & Pawliszyn, J. (2009) *Anal. Bioanal. Chem.* **393**, 781–795. <http://dx.doi.org/10.1007/s00216-008-2375-3>
- (22) de Fátima Alpendurada, M. (2000) *J. Chromatogr. A* **889**, 3–14. [http://dx.doi.org/10.1016/S0021-9673\(00\)00453-2](http://dx.doi.org/10.1016/S0021-9673(00)00453-2)
- (23) Fytianos, K., Drimaropoulou, G., Raikos, N., Theodoridis, G., & Tsoukali, H. (2007) *J. AOAC Int.* **90**, 1677–1682
- (24) Pawliszyn, J. (1999) in *Applications of Solid Phase Microextraction*, J. Pawliszyn (Ed.), Royal Society of Chemistry, Cambridge, UK, pp 3–21. <http://dx.doi.org/10.1039/9781847550149-BX003>
- (25) Aulakh, J.S., Malik, A.K., Kaur, V., & Schmitt-Kopplin, P. (2005) *Crit. Rev. Anal. Chem.* **35**, 71–85. <http://dx.doi.org/10.1080/10408340590947952>
- (26) Falqui-Cao, C., Wang, Z., Urruty, L., Pommier, J.-J., & Montury, M. (2001) *J. Agric. Food Chem.* **49**, 5092–5097. <http://dx.doi.org/10.1021/jf010519u>
- (27) Rodríguez, R., Mañes, J., & Picó, Y. (2003) *Anal. Chem.* **75**, 452–459. <http://dx.doi.org/10.1021/ac025884e>
- (28) Simplicio, A.L., & Boas, L.V. (1999) *J. Chromatogr. A* **883**, 32–42
- (29) Chai, M.K., Tan, G.H., & Asha, K. (2008) *Malay. J. Anal. Sci.* **12**, 1–9
- (30) Beltran, J., Peruga, A., Pitarch, E., & Lopez, F.J. (2003) *Anal. Bioanal. Chem.* **376**, 502–511. <http://dx.doi.org/10.1007/s00216-003-1916-z>
- (31) Lord, H., & Pawliszyn, J. (2000) *J. Chromatogr. A* **885**, 153–193. [http://dx.doi.org/10.1016/S0021-9673\(00\)00535-5](http://dx.doi.org/10.1016/S0021-9673(00)00535-5)
- (32) Kleeger, K.K., Dobberstein, D., Hinrichson, N., Muller, A., & Steinhart, H. (2008) in *Advances in Food Diagnostics*, F. Todra & L.M.L. Nollet (Eds), Wiley-Blackwell, Hoboken, NJ, pp 253–293
- (33) Ai, J. (1997) *Anal. Chem.* **69**, 3260–3266. <http://dx.doi.org/10.1021/ac970024x>
- (34) Risticvic, S., Vuckovic, D., & Pawliszyn, J. (2010) in *Handbook of Sample Preparation*, J. Pawliszyn, & H.L. Lord (Eds), Wiley, Hoboken, NJ, pp 81–102
- (35) Berrada, H., Font, G., & Moltó, J.C. (2004) *J. Chromatogr. A* **1042**, 9–14. <http://dx.doi.org/10.1016/j.chroma.2004.05.017>
- (36) Blasco, C., Font, G., Manes, J., & Pico, Y. (2003) *Anal. Chem.* **75**, 3606–3615. <http://dx.doi.org/10.1021/ac0341362>
- (37) Cai, L., Gong, S., Chen, M., & Wu, C. (2006) *Anal. Chim. Acta* **559**, 89–96. <http://dx.doi.org/10.1016/j.aca.2005.11.048>
- (38) Chai, M.K., Tan, G.H., & Asha, K. (2006) *Malay. J. Chem.* **8**, 67–71
- (39) Dong, C., Zeng, Z., & Li, X. (2005) *Talanta* **66**, 721–727. <http://dx.doi.org/10.1016/j.talanta.2004.12.020>
- (40) Guo, F.-Q., Huang, L.-F., Zhou, S.-Y., Zhang, T.-M., & Liang, Y.-Z. (2006) *Anal. Chim. Acta* **570**, 73–78. <http://dx.doi.org/10.1016/j.aca.2006.04.006>
- (41) Lachenmeier, D.W., Nerlich, U., & Kuballa, T. (2006) *J. Chromatogr. A* **1108**, 116–120. <http://dx.doi.org/10.1016/j.chroma.2005.12.086>
- (42) Lambropoulou, D.A., & Albanis, T.A. (2002) *J. Agric. Food Chem.* **50**, 3359–3365. <http://dx.doi.org/10.1021/jf0112771>
- (43) Lambropoulou, D.A., & Albanis, T.A. (2003) *J. Chromatogr. A* **993**, 197–203. [http://dx.doi.org/10.1016/S0021-9673\(03\)00397-2](http://dx.doi.org/10.1016/S0021-9673(03)00397-2)
- (44) Lambropoulou, D.A., Konstantinou, I.K., & Albanis, T.A. (2007) *J. Chromatogr. A* **1152**, 70–96. <http://dx.doi.org/10.1016/j.chroma.2007.02.094>
- (45) Navalon, A., Prieto, A., Araujo, L., & Vilchez, J.L. (2002) *J. Chromatogr. A* **975**, 355–360. [http://dx.doi.org/10.1016/S0021-9673\(02\)01220-7](http://dx.doi.org/10.1016/S0021-9673(02)01220-7)
- (46) Chai, X., Jia, J., Sun, T., & Wang, Y. (2008) *Chromatographia* **67**, 309–313. <http://dx.doi.org/10.1365/s10337-007-0486-1>
- (47) Hu, R., Hennion, B., Urruty, L., & Montury, M. (1999) *Food Addit. Contam.* **16**, 111–117. <http://dx.doi.org/10.1080/026520399284154>
- (48) Wang, Z., Hennion, B., Urruty, L., & Montury, M. (2000) *Food Addit. Contam.* **17**, 915–923. <http://dx.doi.org/10.1080/026520300750038090>
- (49) Cortés-Aguado, S., Sánchez-Morito, N., Arrebola, F.J., Grenido Frenich, A., & Vidal, J.L.M. (2008) *Food Chem.* **107**, 1314–1325. <http://dx.doi.org/10.1016/j.foodchem.2007.09.033>
- (50) Cortes-Aguado, S., Sanchez-Morito, N., Grenido Frenich, A., Vidal, J.L.M., & Arrebola, L.F.J. (2007) *Anal. Lett* **40**, 2886–2914. <http://dx.doi.org/10.1080/00032710701603934>
- (51) Guillet, V., Fave, C., & Montury, M. (2009) *J. Environ. Sci. Health, B* **44**, 415–422. <http://dx.doi.org/10.1080/03601230902934587>
- (52) Sanusi, A., Guillet, V., & Montury, M. (2004) *J. Chromatogr. A* **1046**, 35–40. <http://dx.doi.org/10.1016/j.chroma.2004.06.035>
- (53) Chen, Y.-L., Su, Y.-S., & Jen, J.-F. (2002) *J. Chromatogr. A* **976**, 349–355. [http://dx.doi.org/10.1016/S0021-9673\(02\)01144-5](http://dx.doi.org/10.1016/S0021-9673(02)01144-5)
- (54) De Koning, S., Janssen, H.-G., & Brinkman, U.A. Th. (2009) *Chromatographia* **69**, S33–S78. <http://dx.doi.org/10.1365/s10337-008-0937-3>
- (55) Pawliszyn, J. (1995) *Trends Anal. Chem.* **14**, 113–122
- (56) Eisert, R., & Pawliszyn, J. (1997) *Anal. Chem.* **69**, 3140–3147. <http://dx.doi.org/10.1021/ac970319a>
- (57) Ouyang, G., & Pawliszyn, J. (2006) *Anal. Bioanal. Chem.* **386**, 1059–1073. <http://dx.doi.org/10.1007/s00216-006-0460-z>
- (58) Wardencki, W., Michulec, M., & Curylo, J. (2004) *Int. J. Food Sci. Technol.* **39**, 703–717. <http://dx.doi.org/10.1111/j.1365-2621.2004.00839.x>
- (59) Zhang, Z., Yang, M. J., & Pawliszyn, J. (1994) *Anal. Chem.* **66**, 844A–853A. <http://dx.doi.org/10.1021/ac00089a001>
- (60) Fernández, M., Padrón, C., Marconi, L., Ghini, S., Colombo, R., Sabatini, A. G., & Girotti, S. (2001) *J. Chromatogr. A* **922**, 257–265. [http://dx.doi.org/10.1016/S0021-9673\(01\)00880-9](http://dx.doi.org/10.1016/S0021-9673(01)00880-9)
- (61) Yu, J., Wu, C., & Xing, J. (2004) *J. Chromatogr. A* **1036**, 101–111. <http://dx.doi.org/10.1016/j.chroma.2004.02.081>
- (62) Cai, L., Xing, J., Dong, L., & Wu, C. (2003) *J. Chromatogr. A* **1015**, 11–21. [http://dx.doi.org/10.1016/S0021-9673\(03\)01328-1](http://dx.doi.org/10.1016/S0021-9673(03)01328-1)
- (63) Farajzadeh, M. A., & Hatami, M. (2004) *Chromatographia* **59**, 259–262
- (64) Zeng, J., Chen, J., Lin, Z., Chen, W., Chen, X., & Wang, X. (2008) *Anal. Chim. Acta* **619**, 59–66. <http://dx.doi.org/10.1016/j.aca.2008.02.013>
- (65) Hu, X., Hu, Y., & Li, G. (2007) *J. Chromatogr. A* **1147**, 1–9. <http://dx.doi.org/10.1016/j.chroma.2007.02.037>
- (66) Djozan, D., & Ebrahimi, B. (2008) *Anal. Chim. Acta* **616**, 152–159. <http://dx.doi.org/10.1016/j.aca.2008.04.037>
- (67) Djozan, D., Mahkam, M., & Ebrahimi, B. (2009) *J. Chromatogr. A* **1216**, 2211–2219. <http://dx.doi.org/10.1016/j.chroma.2008.12.101>
- (68) Djozan, D., Mahkam, M., Ebrahimi, B., & Farajzadeh, M. A. (2010) *Anal. Chim. Acta* **674**, 40–48. <http://dx.doi.org/10.1016/j.aca.2010.06.006>
- (69) Turiel, E., Tadeo, J. L., & Martin-Esteban, A. (2007) *Anal. Chem.* **79**, 3099–3104. <http://dx.doi.org/10.1021/ac062387f>
- (70) Barahona, F., Turiel, E., & Martin-Esteban, A. (2011) *Anal. Chim. Acta* **694**, 83–89. <http://dx.doi.org/10.1016/j.aca.2011.03.052>
- (71) Chen, W., Poon, K.-F., & Lam, M. H. W. (1998) *Environ. Sci. Technol.* **32**, 3816–3820. <http://dx.doi.org/10.1021/es980294c>
- (72) Chai, M.K., Tan, G.H., & Asha, I. (2008) *Anal. Sci.* **24**, 273–276. <http://dx.doi.org/10.2116/analsci.24.273>
- (73) Fytianos, K., Raikos, N., Theodoridis, G., Velinova, Z., & Tsoukali, H. (2006) *Chemosphere* **65**, 2090–2095. <http://dx.doi.org/10.1016/j.chemosphere.2006.06.046>
- (74) Menezes Filho, A., dos Santos, F.N., & de Paula Pereira,

- P.A. (2010) *Talanta* **81**, 346–354. <http://dx.doi.org/10.1016/j.talanta.2009.12.008>
- (75) Zambonin, C.G., Cilenti, A., & Palmisano, F. (2002) *J. Chromatogr. A* **967**, 255–260. [http://dx.doi.org/10.1016/S0021-9673\(02\)00780-X](http://dx.doi.org/10.1016/S0021-9673(02)00780-X)
- (76) Zambonin, C.G., Quinto, M., Vietro, N.D., & Palmisano, F. (2004) *Food Chem.* **86**, 269–274. <http://dx.doi.org/10.1016/j.foodchem.2003.09.025>
- (77) Hu, Y., Yang, X., Wang, C., Zhao, J., Li, W., & Wang, Z. (2008) *Food Addit. Contam.* **25**, 314–319. <http://dx.doi.org/10.1080/02652030701581864>
- (78) Ravelo-Perez, L.M., Hernandez-Borges, J., Borges-Miquel, T.M., & Rodriguez-Delgado, M.A. (2008) *J. Chromatogr. A* **1185**, 151–154. <http://dx.doi.org/10.1016/j.chroma.2008.01.069>
- (79) Sagratini, G., Manes, J., Giardina, D., Damiani, P., & Pico, Y. (2007) *J. Chromatogr. A* **1147**, 135–143. <http://dx.doi.org/10.1016/j.chroma.2007.02.066>
- (80) Natangelo, M., Tavazzi, S., & Benfenati, E. (2002) *Anal. Lett.* **35**, 327–338. <http://dx.doi.org/10.1081/AL-120002533>
- (81) Vazquez, P.P., Mughari, A.R., & Galera, M.M. (2008) *Anal. Chim. Acta* **607**, 74–82. <http://dx.doi.org/10.1016/j.aca.2007.11.027>
- (82) Eisert, R., & Pawliszyn, J. (1997) *J. Chromatogr. A* **776**, 293–303. [http://dx.doi.org/10.1016/S0021-9673\(97\)00332-4](http://dx.doi.org/10.1016/S0021-9673(97)00332-4)
- (83) Otero, R.R., Ruiz, C.Y., Grande, B.C., & Gandara, J.S. (2002) *J. Chromatogr. A* **942**, 41–52. [http://dx.doi.org/10.1016/S0021-9673\(01\)01352-8](http://dx.doi.org/10.1016/S0021-9673(01)01352-8)
- (84) Prosen, H., & Zupancic-Kralj, L. (1999) *Trends Anal. Chem.* **18**, 272–282. [http://dx.doi.org/10.1016/S0165-9936\(98\)00109-5](http://dx.doi.org/10.1016/S0165-9936(98)00109-5)
- (85) Hans-Joachim, H. (2009) *Handbook of GC/MS: Fundamentals and Applications*, Wiley-VCH, Verlag GmbH, Weinheim, Germany, pp 395–406
- (86) Sánchez, A., Millán, S., Sampedro, M.C., Unceta, N., Rodriguez, E., Goicolea, M.A., & Barrio, R.J. (2008) *J. Chromatogr. A* **1177**, 170–174. <http://dx.doi.org/10.1016/j.chroma.2007.10.097>
- (87) Wu, J., Luan, T., Lan, C., Hung Lo, T.W., & Chan, G.Y.S. (2007) *Food Control* **18**, 466–472. <http://dx.doi.org/10.1016/j.foodcont.2005.12.011>
- (88) Wan Ibrahim, W.A., Farhani, H., Sanagi, M.M., & Aboul-Enein, H.Y. (2010) *J. Chromatogr. A* **1217**, 4890–4897. <http://dx.doi.org/10.1016/j.chroma.2010.05.050>

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