

Recent achievements and applications of solid – phase microextraction in pesticide residues analysis in food

Mária Andraščíková, Svetlana Hrouzková

*Institute of Analytical Chemistry, Faculty of Chemical and Food Technology,
Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic
svetlana.hrouzkova@stuba.sk*

Abstract: The current trend in sample preparation methods is devoted to minimizing or eliminating the volume of extractive solvent. In this review, the focus on solid phase microextraction (SPME) as a solvent free sample preparation method for the isolation of pesticides residues in different food matrices is given. To achieve satisfactory extraction efficiency, selection of the fiber coating is an important step in the method development. Here, recent trends in new supporting materials and new fiber coatings development are discussed. Finally, applicability of SPME for the pesticide residues analysis in various food matrices using mainly chromatographic methods is also reviewed.

Keywords: sample preparation, solid phase microextraction, pesticide residues analysis, food

Introduction

Pesticides are synthetic chemicals widely used to prevent and control pest and disease and their applications leads to higher production yields and quality of agricultural crops. One-third reduction in crop yield would be happened if pesticides are not used against pest. However, this process contaminates food and environment by these toxic chemicals (Bagheri et al., 2012). As a result, people are exposed to pesticide residues at low concentrations through the environment, their diets, etc. The extensive and indiscriminate use of pesticides is a major concern because of the potential harm that these compounds can cause to the environment and because of the known or suspected toxic effects in humans. By transformation through the food chain, pesticide residues bioaccumulate in animal and human body and eventually show their adverse effects, like cancer, hormone disruption, disturbances in the immune system, disturbances in the reproductive and endocrine systems, chronic kidney diseases, birth defect, neurological effects and other diseases (Bagheri et al., 2012; Chowdhury et al., 2013; Masiá et al., 2014).

Food analysis is very important for the quality control of products and the determination of additives and toxic contaminants such as pesticides (Viñas et al., 2009). For food samples, pesticide residues have been regulated by several legislative authorities throughout the world, basically concerned with the quality, efficacy and safety in the use of pesticides, however, there is not a global harmonized legislation. Maximum residual limits (MRLs) for pesticides in fruit and vegetables were established by European Union (EU, Regulation

(EC) No. 839/2008) (EC Directive 2005). In general, the MRLs are in the range of 0.01–10 mg/kg, depending on the combination of commodity and pesticide. The MRL value of banned compounds is considered as the minimum limit of detection (LODs) achievable (Masiá et al., 2014).

Food is a very complex matrix, and several procedures are typically used in order to prepare a food sample for the final gas chromatography (GC), liquid chromatography (LC) or other techniques (Kudlejova et al., 2012). Sampling and sample preparation prior to chromatographic analysis is one of the most critical steps of the whole analytical processes, depends on the type of matrix, especially for the analysis of trace levels of analytes in complex matrices (Zhao et al., 2011; Kudlejova et al., 2012). Consequently, there is a need to develop, time saving, fast, green and accurate analytical procedures capable of detecting low concentrations of pesticides in a variety of food matrices (Souza-Silva et al., 2013). In order to prepare a representative sample, all kind of matrices need to be homogenized prior to the isolation of the target analytes from the examined matrix (Kudlejova et al., 2012).

Efficient sample preparation requires minimal analyte loss; analyte recovered in a good yield; efficient removing of coexisting components; to avoid problems in chromatography systems; the procedure can be performed conveniently and quickly; and inexpensive. Furthermore, use of harmful chemicals and large amounts of solvent in the sample preparation step cause environmental pollution and health hazards for operators, and extra-operational costs for waste treatment (Kataoka et al., 2009; Martins et al., 2012).

Among conventional methods of sample preparation at the determination of pesticide residues in food, liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are the most conventional and still frequently used sample preparation method (Filho et al., 2008). LLE is time-consuming, tedious, and often requires large quantities of toxic organic solvents. SPE is difficult to be applied widely in complex sample matrix. SPE may be faster than LLE, but in the elution step, SPE column still requires to be washed by organic solvents, and the presence of particulate matter in food samples or biological samples easily results in plugging of the cartridges (Wang et al., 2008). Recent trends in the sample preparation have focused on miniaturization, automation, high throughput performance, on-line coupling with analytical instruments and low-cost operations through extremely low or no solvent consumption in order to minimize the environmental effect (Moliner-Mratinez et al., 2009; Andraščiková et al., 2015). A number of sample preparation methods have been developed for the isolation and enrichment of analytes from different samples. In recent years, many applications in the field of pesticide residues analysis have been performed using liquid phase microextraction (LPME) such as single drop microextraction (SDME), dispersive liquid-liquid microextraction (DLLME) and hollow fiber liquid phase microextraction (HF-LPME) (Andraščiková et al., 2015). As an alternative, SPME has important advantages because it is a simple and rapid technique which minimizes the sample handling (Ruiz del Castillo et al., 2012). SPME requires little or no organic solvents, is easily automated, and can also improve the limits of detection. SPME encompasses sampling, extraction, preconcentration and introduction of the sample extract into the system of analyses in a single uninterrupted process, thus avoiding contamination of the sample extract (Filho et al., 2008).

The objective of this work is to present an overview of the recent achievements of SPME for the isolation of pesticides from different food matrices. New supporting materials and techniques for the preparation of SPME fiber coatings are mentioned and discussed together with different extraction and desorption modes of the SPME method. Combination of SPME with analytical instrumentation for pesticide residues analysis of food in order to reach fast and simple solventless “green” method is evaluated.

Solid phase microextraction principle

Solid-phase microextraction was introduced and developed by Pawliszyn (Arthur et al., 1990). The

technique is based on the partition of the analyte between the sample matrix and a stationary phase that is a fibre coated with an extracting liquid (polymer) or solid (sorbent) phase and housed in the commercial holder (Melo et al., 2012). Equilibrium is reached between the concentration of the analyte in sample and the concentration of analyte sorbed on the fiber, depending on the distribution coefficient. After that, desorption of the analytes can be performed thermally into a heated injector for GC determination or with a solvent, mainly when LC is used (Pereira et al., 2014). Fiber is portable and the whole technique is easily automated. Except for special applications, SPME methods use existing injectors on GC instruments, and analytes are thermally desorbed into the inlet. In LC analysis, the desorption interface typically consists of a standard six-position valve with a special fibre desorption chamber and desorption is performed into the mobile phase (Kudlejova et al., 2012).

The main advantage of the SPME procedure with respect to other techniques is the fact that it uses no or little volume of extraction solvent. The SPME approach is relatively simple (sampling, extraction and sample concentration are integrated in one step), fast and cheap. SPME methods are suitable for liquid, solid and gaseous samples and typically use only small sample volumes (Kudlejova et al., 2012). SPME is an alternative extraction method to traditional techniques, due to solvent consumption, blanks reduction and a decrease in extraction time. This method does not require complete removal of the analyte from the liquid matrix and can be used for a wider range of applications than other techniques such as solid phase extraction (SPE), which requires an exhaustive extraction (Kataoka et al., 2009). Owing to its convenience, almost solvent-free operation and low cost, it has gained wide applicability as an analytical technique (Melo et al., 2012).

Parameters affecting SPME performance

Several factors can influence the SPME efficiency. During the extraction step, the nature and the thickness of the fiber, the ionic strength and the pH of the aqueous sample, the stirring conditions and the temperature and time of the extraction must be optimized. During the desorption step, temperature of the GC injector and desorption time must be considered (Martins et al., 2012).

Fibers coating in SPME

Selection of a suitable fiber coating is the first step in SPME method development. The SPME fiber comprises a supporting substrate and thin layer of

sorbent material. Fused-silica fiber has been successfully used as supporting substrate since the first introduction of SPME technology (Feng et al., 2013). As the extraction efficiency of SPME is strongly dependent on the distribution constant of the target chemical between the fiber coating and sample matrix, the fiber coating is the most important and key factor in SPME (Yang et al., 2013; Ghaemi et al., 2014). Up to now, several coating fibers are commercially available for SPME, including polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), carboxen (CAR), carbowax (CW), and their copolymers (Luo et al., 2012). The different fiber materials offer a range of polarities to extract volatile and semi-volatile compounds. The materials have also been combined to create fibers able to sample compounds with a wider range of properties than if a single material had been used (Heaven et al., 2012). Four coating materials with different polarity (PA, PDMS, PDMS-DVB, DVB-CAR-PDMS and CAR-PDMS) were evaluated at the SPME extraction of 14 pesticides in mango fruits (Filho et al., 2008). PA coating was able to extract great number of pesticides and also capable to concentrate larger amounts of each extracted pesticide.

Among the commercial fibres, PA, PDMS/DVB and PDMS were evaluated (Song et al., 2014). PA was well suited for the diphenylamine determination when coupled with gas chromatography-mass spectrometry (GC-MS) and provided good sensitivity and dynamic range. Extraction performance of four different SPME coating, such as PDMS, PDMS/DVB, CW/templated resin (CW/TPR) studied and PA for pesticides with log P (partition coefficient) ranged from 0.8 to 4.12 (Melo et al., 2012). CW/TPR showed the best extraction performance for pesticides with higher value of log P (higher than two). Although these commercial fibers have been successfully applied in many fields, they still have some drawbacks such as expensive, thermal, mechanical and/or chemical instability, insufficient selectivity, and fragility of the fused-silica substrate, limited range of polarity and reuse times, which largely restricts the application of SPME (Luo et al., 2012). Their relatively low recommended operating temperature (generally in the range 200–270 °C) causes incomplete sample desorption and memory effect problems. In addition, swelling in organic solvent, relatively high thickness and difficult preparation in a routine laboratory are the further disadvantages of the studied fibers (Feng et al., 2013; Saraji et al., 2013).

Numerous efforts have been made to produce novel SPME fibers with improved durability and satisfactory extraction capacity (Feng et al., 2013). Studies have

been focused on fabricating low cost, simple, robust and long-life fiber for the target analytes. A variety of methods for the production of fibers have been developed such as sol-gel, and physical and electrochemical polymerization (Korba et al., 2013). Sol-gel technology can provide efficient incorporation of organic components into the polymeric structures in solution under the relatively mild conditions. Furthermore, strong chemical bonding between the polymer coating and the surface of fused-silica fiber improves the properties of SPME fibers (thermal stability, solvent stability, and lifetime). The coating porosity introduced by the sol-gel method enlarges the surface area of the fiber and allows for the utilization of thinner coatings to obtain higher enrichment during the extraction process (Wang et al., 2008; Ghaemi et al., 2014). Another advantageous is possibility to trap compounds containing different functional groups into the film by simply adding them into the sol-gel solution to prepare special SPME coating (Saraji et al., 2013).

Sol-gel technology has been applied in SPME as fibre coating for the extraction of various pesticides from food and environmental matrices (Cai et al., 2006; Wang et al., 2008; Ibrahim et al., 2010; Saraji et al., 2013). Three kinds of vinyl crown ether polar fibers, 3'-allyl benzo-15-crown-5 (B15C5), 4'-allyl dibenzo-18-crown-6 (DB18C6) and allyloxy ethoxymethyl-18-crown-6 (PSO18C6) were prepared by a sol-gel method and compared with commercial PA and PDMS-DVB fibers (Cai et al., 2006). New coatings showed higher extraction efficiency and sensitivity for organophosphorus pesticides (OPPs). Specifically, the B15C5 coating with larger polarity and selectivity than other studied fibers was the most effective for the target analytes. The higher extraction efficiency co-poly(hydroxy-terminated silicone divinylbenzene) (OH-TSO/DVB) fiber prepared by sol-gel technology in comparison to commercial available fibers was reported by Wang et al., 2008. Higher extraction efficiency of sol-gel derived OH-TSO/DVB fiber is attributed to the three dimensional porous network in the coating structure and also the polarizable phenyl groups in this fiber. The prepared fiber was applied to determine OPPs in pakchoi samples.

Despite advantages of the sol-gel technology, its SPME application has been limited due to the fragility of the silica fiber applied as the base of sol-gel technology (Saraji et al., 2013).

The electrochemical method for preparing SPME fibers is simple, low cost, reproducible and convenient. It is especially suitable for fibers with metal wires as supporting substrate, because the metallic support can be directly used as one of the electrodes (Feng et al., 2013).

Polypyrrole (Ppy)/sol-gel coating fiber was prepared through electrochemical decomposition on stainless steel wire for the determination of OPPs in vegetable samples such as cucumber and lettuce (Saraji et al., 2013). Extraction efficiency of the Ppy/sol-gel composite fiber on a stainless steel wire was compared to Ppy fiber without sol-gel and two commercial fibers (PDMS, PDMS/DVB). The Ppy/sol-gel composite provides better efficiency than other studied fibers. The affinity of the Ppy/sol-gel coating for the analytes is due to the phenyl and hydrophilic groups in the coating that enhanced the π – π interaction, hydrogen bonding, and dipole–dipole interactions with the selected pesticides. Moreover, the sol-gel coating technique provides a porous structure, which increases the surface area of the fiber and affords a fast mass transfer rate in the film (Saraji et al., 2013). PPy fiber for HS-SPME was fabricated by electrochemical polymerization onto a steel wire and in-situ produced fiber coating was proven to have high extraction efficiency for endocrine disruptor pesticides (Korba et al., 2013). Even after 250 usages, the fiber can still be used sensitively with a reasonable precision.

Recently, new laboratory-made coating materials have been developed for SPME, such as molecularly imprinted polymers (MIPs), ionic liquids (ILs) and carbon nano tubes (CNTs). The vast majority of MIP-coated fibers, by far, are synthesized by the co-polymerization method, using methacrylic acid and its derivatives as monomers (Wang et al., 2013). Monolithic SPME fiber on the base of MIP for the selective extraction of triazine herbicides in rice and onion was prepared by copolymerization of methacrylic acid-ethylene glycol dimethacrylate imprinted with atrazine (Djozan and Ebrahimi, 2008).

A sol-gel technique was applied for the preparation of water-compatible MIP for SPME using diazinon as template and polyethylene glycol as functional monomer (Wang et al., 2013). The MIP-coated fibers had a life-time of more than 100 uses for headspace SPME of OPPs without a substantial change in the properties of the coating (Wang et al., 2013). IL-calixarene coated SPME fiber for the extraction of triazines from fruit and vegetable samples was reported by Tian et al., 2014. Developed SPME fiber in connection with GC equipped by flame ionization detector provided selective and sensitive technique for monitoring triazines in fruit and vegetable samples. Wu et al., 2010, prepared SPME fibre using a single-walled carbon nanotubes (SWCNTs) as a stationary phase and the efficiency of the fiber was compared with commercial PDMS and PA fibres. SWCNTs fiber had high extraction efficiency for studied pesticides with commercial

fibres and could be used for more than 70 times without decrease of efficiency.

The recent development of novel SPME fibers has partly been attracted to flexible metal-wire supporting substrates to replace of the fragility fused-silica fiber applied as supporting material. These new materials, including stainless steel, aluminum, zinc, copper, gold, platinum, silver, and titanium, are of strong physical strength, and can be handled with greater convenience. Due to the quite different physicochemical properties of these metal wires from fused-silica fiber, there has been a great variety of preparation methods of the metal-wire supported SPME fibers (Feng et al., 2013). Stainless steel wire as a supporting substrate in combination with sol-gel technology was shown flexible, unbreakable, with higher mechanical strength than silica fiber (Saraji et al., 2013). Stainless steel wire was also used as a support for dodecyl sulphate-doped polypyrrole (Ppy-DS) coating (Korba et al., 2013) and for PDMS coating (Bagheri et al., 2012).

Majority of published papers in the field of pesticide residue analysis in food samples were performed using commercially available fibers such as PDMS, PDMS-DVB (Table 1, 2).

Sampling mode

In the last several years, SPME has been widely applied to the extraction of different classes of pesticide residues in a wide variety of food matrices (Table 1, 2). Direct immersion SPME (DI-SPME), where the extraction phase is placed directly in contact with the sample, is most frequently used for isolation of pesticide residues from fruit, vegetable, honey, milk and wine samples. Therefore, a pre-treatment step is essential prior to DI-SPME. As the fiber coating is in direct contact with the sample phase, it has high extraction efficiency, and it is suitable for semivolatile compounds (Yang et al., 2013). Many types of pesticides have been determined in food matrices using the DI-SPME method such as organochlorine (Moliner-Martinez et al., 2010), OPPs (Capobianco et al., 2005; Saraji et al., 2013), carbamates (Song et al., 2013), triazoles (Souza-Silva et al., 2008), triazines (Djozan et al., 2008; Tian et al., 2014) and strobilines (Viñas et al., 2009).

Alternatively to DI, in headspace-SPME (HS-SPME) mode, the extraction phase is placed in the headspace above the sample rather than immersed into the sample. HS is the preferred method for extraction of complex matrices, since no direct contact with sample protects the fiber coating from being damaged by high molecular mass and other non-volatile interferences present in the sample matrix. Albeit, HS-SPME is not suitable for all the cases; major limitations include low rates of extraction

for poorly volatile or polar analytes (Souza-Silva et al., 2013). HS-SPME has been predominantly used for the determination of OCPs (Dong et al., 2005; Cai et al., 2006; Chai et al., 2009) and OPPs (Cai et al., 2006; Chai et al., 2009; Ibrahim et al., 2010; Wang et al., 2013; Sang et al., 2013) in different food matrices.

The majority of food applications were performed in the DI mode (Table 1), while the HS mode (Table 2) is more frequently used in combination with fibers prepared by sol-gel techniques. SPME extraction by DI mode was predominantly used to extract pesticide residues from fruit samples using PDMS fibre. HS mode was used for determination of OPPs in cow milk without previous cleaning step (Rodrigues et al., 2011). Determination of OPPs in milk in DI mode has been performed after adjusting pH with buffer and centrifugation (Cardeal et al., 2006). Filho et al., 2008 compared both, DI and HS extraction modes, using PA fiber for determination of pesticides residues in mangoes. HS extraction was efficient in extracting the more volatile compounds, such as OPPs and pyrethroids. In DI mode were successfully extracted all studied pesticides with lower sensitivity than HS mode. Extraction of OPPs in water and vegetable samples using fiber coated with polypyrrole/sol gel composite was performed in DI mode (Saraji et al., 2013). HS mode was used for extraction of organochlorine pesticides in wine using dodecylsulfate-doped polypyrrole (Ppy-DS) fiber (Korba et al., 2013). Selection of operating in HS or in DI mode depends on the volatility of the analytes and the matrix characteristics (Martins et al., 2013).

Magnetic stirring

Agitation of sample can accelerate mass transfer of the analytes between the aqueous sample and the SPME fiber and reduces the time required to reach equilibrium (Wu et al., 2010). At higher stirring rate (>800 rpm) in DI air bubbles can occur on the fiber surface resulting in lower extraction (Saraji et al., 2013). Low stirring rate (250 rpm) can be used in DI provided that the signal for pesticides was decreased at higher stirring rate (Filho et al., 2008). The most frequently used stirring rate for HS mode was 600 rpm (Rodrigues et al., 2011; Korba et al., 2013; Wang et al., 2013), nevertheless some studies were performed using lower (120 rpm) (Ibrahim et al., 2010) or higher stirring rate (800 rpm) (Chai et al., 2009). For HS mode stirring rate 600 rpm was used for determination of OCPs pesticides in radish (Dong et al., 2005). In DI mode stirring rate was often higher than 500 rpm up to 1700 rpm (Chai et al., 2009).

Ionic strength and pH adjustment

In many cases, an addition of NaCl is used to increase ionic strength of sample solution. The addition of salt may lead to a decrease of the extraction efficiency (Campillo et al., 2006). The decrease of extraction efficiency for OCPs and OPPs when the portion of NaCl exceeds 10 % because of predominant salt interaction with the analyte in the solution could be observed (Chai et al., 2009).

Modification of the ionic strength prior the solvent extraction or the SPME extraction did not affect significantly the instrumental response obtained (Cortés-Aguado et al., 2008). It was observed that for some compounds the sensitivity was increased by a salting-out effect during the solvent extraction (lindane, malathion, iprodione) but for others (bromopropylate, buprofezin, chlorpyrifos-methyl) their instrumental response was reduced especially when the addition of salt was done just before the SPME extraction. It was attributed to a negative influence of the deposition of salt on the coating material. Higher extraction efficiency in HS mode adding 1 g of potassium sulphate into the radish sample instead of NaCl was observed (Dong et al., 2005).

In the DI determinations, pH adjustment was also evaluated. Sodium hydroxide (Song et al., 2013; Munitz et al., 2013) and phosphate buffer (Campillo et al., 2006; Viñas et al., 2009) were predominantly used for the pH adjustment. Some determinations were performed at pH 7 (Djozan et al., 2008; Munitz et al., 2013) and lower (Cardeal et al., 2006; Viñas et al., 2009; Wu et al., 2010; Song et al., 2013). SPME of pesticides residues in fruit and vegetable (Tian et al., 2014) at pH 8 was performed. Nevertheless, pH 9.5 was used for the SPME extraction of pesticide residues in wine and subsequently for the determination by micellar electrokinetic chromatography (MEKC). Maximum selectivity at pH 5.5 for the determination of pesticides residues in tea was obtained by Wu et al., 2010. pH adjustment in SPME for the determination of pesticide residues in apples showed no significant influence on the extraction efficiency (Hu et al., 2008).

Extraction temperature

It is known that sample temperature has a double influence; high temperature increases the diffusion coefficient of analytes in aqueous medium and shortens the extraction time (Campillo et al., 2006). On the other side, high extraction temperature normally improves extraction rate, but simultaneously reduces the distribution coefficient and extraction sensitivity (Wu et al., 2010). Extraction temperature for HS-SPME determination of pesticide residues in fruits and vegetable should be optimized (Chai

et al., 2009). The extraction temperature of 60 °C was found to be the optimum. This is due to the fact that the extraction efficiency decreases when the extraction temperature exceeds 60 °C as a result of the degradation of the pesticides with increasing water vapor pressure in a gas tight vial and the formation of air bubbles. Also, SPME in HS mode was performed at room temperature (Ravelo-Peréz et al., 2007). Extraction efficiency HS-SPME for OCPs in radish was increasing up to 70 °C but decreased above 70 °C (Dong et al., 2005). Extraction efficiency of SPME in DI mode for multiclass pesticides in tea reached maximum at 50 °C (Wu et al., 2010). Extraction temperature is less important when working by DI of the fiber than HS mode. In general, higher extraction temperatures are used in HS mode in comparison to DI mode maintaining the same fiber and thickness. The most frequently used temperature in HS mode was 70 °C and in DI mode was 50 °C and most often at room temperature.

Extraction time

Extraction time is an important parameter for the extraction performance of analytes since SPME is an equilibrium-based technique. Generally, extraction efficiency is improved with the increase of extraction time (Wu et al., 2010). Extraction time has a direct relationship with the thickness and type of fiber coating, and the amount analyte extracted (Saraji et al., 2013).

Desorption conditions (desorption temperature, time and solvent)

The aim of thermal desorption is to ensure the vaporization of each pesticide and to avoid the thermal degradations and also to protect the fiber from degradation (Cortés-Aguardo et al., 2008). The analyte can be desorbed effectively under a higher temperature in a shorter time, but the stability and the lifetime of the fiber will be affected and the analyte may be decomposed if the desorption temperature is too high (Dong et al., 2005).

Therefore, thorough optimization of conditions is essential. Overall, 2 min were sufficient to allow the complete desorption of the analytes at 270 °C using laboratory made calix[4]arene fiber to determine OPPs in radish (Dong et al., 2005). Desorption time 3 min at 280 °C was sufficient to complete desorption of 3 OPPs from the fiber, but 4 min were chosen due to better reproducibility (Saraji et al., 2013). The desorption of 6 OCPs at desorption temperature of 200 °C and desorption time of 5 min was obtained by Korba et al., 2013. The complete desorption of analytes from the fiber enhances the detector response and eliminates memory effect (Filho et al., 2008).

Liquid desorption of analytes was performed using methanol (Ravelo-Peréz et al., 2007; Song et al., 2013), methanol in combination with water (Sagratini et al., 2007; Hu et al., 2008; Melo et al., 2012), and acetonitrile (Bagheri et al., 2012). Hu et al., 2008 performed liquid desorption using mobile phase (methanol:water, 50 : 50, v/v) as the desorption solvent for 5 min. Liquid desorption using mixture methanol:water (70 : 30) for 15 min was performed by work Blasco et al., 2011. The most frequently used desorptive technique in SPME for pesticide residues analysis is thermal desorption, especially in a combination with GC. Liquid desorption was used in the combination with HPLC (Sagratini et al., 2007; Hu et al., 2008; Blasco et al., 2011; Melo et al., 2012; Song et al., 2013), capillary electrophoresis (Hernández-Borges et al., 2005) and MEKC (Ravelo-Pérez et al., 2007). Despite, the use of liquid desorption with subsequent GC-MS analysis was reported (Bagheri et al., 2012).

To obtain the satisfactory extraction efficiency all mentioned parameters must be optimized.

Sample pretreatment

The pretreatment of the sample prior to SPME is the first step in a method development. Sample pretreatment is necessary to protect the fiber coating and avoid the fouling of the extraction phase by irreversible adsorption of macromolecules from the sample matrix, which could not only lead to a substantial decrease in the fiber lifetime, but also could possibly change the coating extraction properties (Souza-Silva et al., 2013). The simplest possible pretreatment was centrifugation and subsequently dilution (Sagratini et al., 2007) or filtration applied for juice samples (Hernández-Borges et al., 2005). Fruit and vegetable samples were homogenized, extracted by liquid-liquid extraction, diluted and centrifuged. However, some complex matrices like milk adversely affect DI-SPME performance in such circumstances. Fouling the SPME fiber reduces reproducibility of results due to large molecular weight compounds within the matrix either attaching to the fiber or hindering smaller compounds reaching the fiber. Fouling of the SPME fiber can be lessened by removing matrix components (e.g. saponifying milk fats), dilution of the sample, the adjustment of pH or increasing the solution salt content (Saraji et al., 2013).

Interface to analytical instrumentation

SPME can be conveniently interfaced to various analytical instruments such as GC (Wu et al., 2010; Tranchida et al., 2013), LC (Sagratini et al., 2007),

HPLC (Hu et al., 2008; Song et al., 2013), MEKC (Ravelo-Pérez et al., 2007) and electrophoresis (Hernández-Borges et al., 2005) with different detectors. The choice of the separation/detection system will largely depend on the goals of the analysis (Kudlejova et al., 2012b). Analysis of pesticides in vegetables has for many years been performed by use of GC especially coupled with nitrogen phosphorus detector (NPD), electron capture detector (ECD) and mass spectrometry (MS) or MS/MS. At present, MS is the most applicable due to the identification power. However, HPLC coupled to other less powerful detectors, that are easier to acquire and use, is preferable for polar, low volatile and/or thermolabile compounds that are not directly determinable by GC (Melo et al., 2012).

To date, SPME coupled with GC has been widely investigated for the determination of pesticide residues in different fruit matrices (Table 1, 2). SPME was more frequently used in connection with GC in comparison with LC or HPLC because of its solvent-less nature. When coupled with GC, SPME can integrate sampling, isolation, enrichment and injection steps, which makes the analysis much more convenient (Luo et al., 2012), in addition, it provides higher sensitivity, selectivity and better detection limits than LC in pesticide analysis, while CE provides a faster alternative to the chromatographic techniques.

LODs for SPME in HS mode obtained by GC-MS varied from 0.01 µg/kg (OPPs in fruit) to 2.88 µg/kg (OPPs in vegetable). Values of LODs from 0.005 µg/kg (strobilines in baby food) to

88 µg/kg (triazine herbicides in rice and onion) were obtained using SPME in DI mode.

GC coupled with ECD was used in a combination with SPME in HS mode for the determination of OPPs or OCPs in fruit and vegetable (Dong et al., 2005; Chai et al., 2009; Ibrahim et al., 2010), also, in DI mode for the determination of OCPs in biota samples (Korba et al., 2013) or for determination of boscalid in blueberries (Munitz et al., 2013). LODs varied from 0.0014 µg/kg (OCPs in radish) to 4.8 µg/kg (OPPs in fruit samples) utilizing SPME in HS mode as sample preparation method. In DI mode, LODs varied from 0.3 to 7.1 µg/kg (OCPs in biota samples). FPD (flame photometric detector) for determination of eight OPPs in fruit and vegetable samples with LODs in the range of 0.003–0.076 µg/kg was used by Cai et al., 2006.

The MS detector in combination with LC after SPME in the DI mode was used for the determination of carbamates and phenylurea in fruit juice (Sagrati et al., 2007) and OPPs and carbamates in honey samples (Blasco et al., 2011) with LOD 1–60 µg/kg.

HPLC was the most often used technique with the diode array detector in combination with SPME in the DI mode (Melo et al., 2012; Song et al., 2013). Limits of detection varied from 0.09 µg/kg (carbamate in apples) to 1540 µg/kg (multiclass pesticides in lettuce). The diode array detection was used with MEKC for the determination of multiclass pesticides in wine with LOD 54–113 µg/kg.

SPME in combination with MEKC and DAD was studied for determination of 12 multiclass pesticides in wine with LOD from 54 µg/kg to 113 µg/kg.

Tab. 1. Applicability of solid phase microextraction (SPME) method in direct immersion mode (DI) for the determination of pesticide residues in different food matrices.

Sample	Pesticides	Pretreatment	Fiber	Extraction conditions	Analytical technique	Real samples positive findings	LOD (LOQ) [µg/L] [µg/kg]	Ref.
Tea	13 multiclass pesticides	grinding, sieving, 1 g homogenized sample extracted with 10 mL acetone, centrifugation, 1 mL supernatant diluted to 20 mL with NaCl solution (15 % NaCl, w/v, pH 5.5)	SWCNTs	600 rpm, 50 °C, 40 min	TD-GC-MS	1590 µg/kg (chlorfenapyr) 17–54 µg/kg (λ-cyhalothrin)	0.027–0.23	Fu et al., 2010
Brewed tea	30 pesticides	2 mL tea sample	100 µm PDMS	750 rpm, 60 °C, 5 min	TD-GC-QqQ MS	-	0.004–4.76 (0.014–15.87)	Tranchida et al., 2013
Apple and orange juice	5 multiclass pesticides	filtration, centrifugation, 6 mL sample + 1.8 g NaCl (31 %, w/v), pH 6 adjusted with 0.1 mol/L NaOH	60 µm PDMS/DVB	800 rpm, ambient temperature, 150 min	LD (200 µL methanol, 200 µL 0.4 M HAc) CE-UV	15–25.5 µg/L	3.1–47	Hernández-Borges et al., 2005

Sample	Pesticides	Pretreatment	Fiber	Extraction conditions	Analytical technique	Real samples positive findings	LOD (LOQ) [µg/L] [µg/kg]	Ref.
Fruit juice (orange, apple cherry, strawberry)	6 carbamates, 3 phenylureas	centrifugation, 0.5 mL supernatant diluted with 0.5 mL water + 0.3 g NaCl	50 µm CW/TPR, 60 µm PDMS/DVB, 85 µm PA	1000 rpm, 15 min	LD (methanol: water, 70 : 30, v/v) LC-MS	–	1–10	Sagratini et al., 2007
Fruit juice (orange, pineapple, peach)	54 multiclass pesticides	1 mL sample + 1 mL ethyl acetate, shaken, 0.5 mL ethylacetate extract evaporation, 1 mL water:acetone (9 : 1, v/v) addition	100 µm PDMS 65 µm PDMS/DVB	ambient temperature, 10 min	TD-GC-MS	48 µg/L (chlorpyrifos)	0.4–19.6	Córtes-Aguardo et al., 2008
Apples	Carbendazim, thiabendazole	25 g mashed apples + 20 mL water, centrifugation, resultant supernatant + 10 mL water, aliquot 4 mL for SPME	60 µm PDMS/DVB	1100 rpm, 20 °C, 35 min	LD (methanol : water, 50 : 50, v/v) HPLC-FD	33–520 µg/kg	5 (carbendazim) 3 (thiabendazole)	Hu et al., 2008
Apples	5 carbamate pesticides	2 g of pulp homogenized sample, ultrapure water addition with salt concentration of 16 % (w/v), pH adjusted to 5.5	CNTs-HF	950 rpm, 60 min	LD – 25 µl methanol HPLC-DAD	methiocarb	0.09–6 (0.4–11)	Song et al., 2013
Blueberries	Boscalid	extraction of 10 g blended sample with water, vortex, pH adjusted to 7 with NaOH, centrifugation, filtration	100 µm PDMS	1500 rpm, 15 min	GC-µECD	–	1.33 (4.42)	Munitz et al., 2013
Grapes and wine	Azoxystrobin, kresoxymethyl, trifloxystrobin	grapes crushed and filtered, 3 mL sample + 300 mg Na ₂ SO ₄	100 µm PDMS	50 °C, 30 min	TD-HPLC-DAD	–	73–181	Abdulráuf et al., 2013
Grapes and strawberries pulps	10 triazole fungicides	homogenization, 9 g fruit pulp	65 µm PDMS/DVB	500 rpm, 50 °C, 15 min	GC-ToFMS	9–500 µg/kg	grapes (0.25–5) strawberries (0.5–5)	Zhao et al., 2011
Mango	14 multiclass pesticides	homogenization, 3 g sample + 10 mL isopropyl alcohol:water (20 : 80, v/v) with 5 % NaCl and pH 3, stirring at 1000 rpm for 10 min, centrifugation, upper layer completed with alcohol:water mixture to 10 mL	85 µm PA	250 rpm in alternate cycles, 50 °C, 30 min	TD-GC-MS	12.67–93.36 µg/kg	1–10	Filho et al., 2008
Cucumber	7 multiclass pesticides	chopped, homogenized, diluted with 25 mL water and shaken, mixture was transferred into a 50 mL volumetric flask made up with water, centrifugation, 1 mL for SPME	stainless steel wire coated by PDMS	150 rpm, 30 min	LD (600 µL acetonitrile) GC-MS	55–82 µg/kg (diazinone) 114 µg/kg (malathion) 90 µg/kg (penconazole) 187 µg/kg (phosalone)	8–60	Bagheri et al., 2012
Cherry tomato and strawberry, cucumber, garlic sprout, cole, cabbage, and tomato	4 triazines	2 g crushed sample+20 mL acetonitrile, extraction in water bath, ultrasonic bath, centrifugation, extraction with supernatant obtained by centrifugation repeated, concentration, dissolution with 1 mL methanol, reconstitution to 10 mL with NaH ₂ PO ₄ buffer (pH 8.0), centrifugation, filtration	IL-calix-arene-coated fibres	40 °C, 20 min	GC-FID		3.3–13	Tian et al., 2014

Sample	Pesticides	Pretreatment	Fiber	Extraction conditions	Analytical technique	Real samples positive findings	LOD (LOQ) [$\mu\text{g/L}$] [$\mu\text{g/kg}$]	Ref.
Tomato	25 multiclass pesticides	200 g sample + 240 mL acetonitrile:water (50 : 50, v/v) (for pyrethroids), 200 g sample + 240 mL water (for other pesticides), microwave heating, irradiation, cooling to room temperature, centrifugation, 9 mL aliquots of supernatant for SPME	60 μm PDMS/DVB (for pesticide soluble in water), 100 μm PDMS (for pyrethroids)	500 rpm, ambient temperature, 30 min (pyrethroids), 45 min (other pesticides)	TD-GC-MS	1–860 $\mu\text{g/kg}$	0.01–7.62	Guillet et al., 2009
Tomato	19 chlorinated pesticides	4 g homogenized sample + 18 mL ultrapure water, sonication	100 μm PDMS	400 rpm, 28 $^{\circ}\text{C}$, 30 min	TD-GC-ECD	without positive findings	0.5–8 (5–30)	Mariani et al., 2013
Lettuce	10 multiclass pesticides	–	50 μm CW/TPR	1000 rpm, room temperature, 30 min	LD (60 μl methanol : water (9 : 1)) HPLC-DAD	were not detected 14 days after sprayed	280–1540	Melo et al., 2012
Cucumber, lettuce	3 OPPs	2 g homogenized sample + 2 mL water, ultrasonication for 10 min	stainless steel fiber coated with Ppy/sol gel composite film	800 rpm, 30 min	TD-GC-NPD	without positive findings	0.0015–0.01	Saraji et al., 2013
Cabbage, kale, mustard	11 OPPs	0.5 g chopped and homogenized sample + 2 mL methanol/acetone (1 : 1, v/v) + 1 mL NaCl solution (10 %, w/v, dilution to 10 mL with water)	85 μm PA	1275 rpm, room temperature, 30 min	TD-GC-FPD	mustard 0.22–1.83 (chlorpyrifos)	0.01–0.14 (0.03–0.42)	Sapahin et al., 2015
Onion, rice, bran	12 triazine herbicides	onion crashed to produce juice, ultrasonic bath, centrifuged, 3 mL supernatant for SPME, rice and bran dried and powdered + 12.5 mL methanol, ultrasonic water bath, filtration, evaporation, dissolved with 3 mL methanol, pH 7 adjusted by phosphate buffer	atrazine-MIP fiber	500 rpm, room temperature, 25 min	TD-GC-MS	onion 91.1–485 $\mu\text{g/L}$	20–88	Djozan et al., 2008
Rice, maize, onion	12 triazine herbicides	54 g crushed onion and maize stirred in a ultrasonic bath and centrifuged, 3 mL supernatant solution filtered 10 g dried and powdered rice seeds + 12.5 mL methanol dilution up to 25 mL with ultrapure water, ultrasonication, filtration, 5 mL filtered solution dried under N_2 + 3 mL methanol to dissolve residues and diluted up to 10 mL with ultrapure water	ametryn-MIP	room temperature, 20 min	TD-GC-MS		onion and maize 10–90 rice 30–230	Djozan et al., 2009
Baby food (carrots, vegetables, chicken with rice, chicken and lamb with vegetables)	7 strobilurin fungicides	25 g baby food dilution up to 10 mL water, sonication, filtration, 8 mL sample solution + 1 mL 0.15 M phosphate buffer pH 5 + water to adjust to final volume 14 mL	60 μm PDMS/DVB	1700 rpm, 60 $^{\circ}\text{C}$, 40 min	TD-GC-MS	–	5–30	Viñas et al., 2009

Sample	Pesticides	Pretreatment	Fiber	Extraction conditions	Analytical technique	Real samples positive findings	LOD (LOQ) [$\mu\text{g/L}$] [$\mu\text{g/kg}$]	Ref.
Fresh fish, potatoes, guava, coffee	6 OPPs	homogenized sample: 0.5 g fish + 16 mL water 0.5218–0.6088 g potato + 16 mL water 0.5 g guavas + 16 mL water 0.1805–0.1842 g coffee grains and leaves + 16 mL water	100 μm PDMS	30 °C, 40 min	TD-GC-NPD	0.02–0.26 $\mu\text{g/kg}$	0.005–8.374	Capobiango et al., 2005
Biota samples (mussels and cockles)	9 OCPs	0.1 g lyophilized sample + 0.4 g C18 homogenization, SPE – desorption: 1.2 mL MeCN, dilution with 2.6 mL water	65 μm PDMS/DVB	continuous stirring, 45 min	TD-GC-ECD	mussels 1.8–2.9 $\mu\text{g/kg}$ (hexachlorobenzene)	0.3–7.1	Moliner-Martinez et al., 2009
Honey	12 OPPs, carbamate insecticides	5 g sample + 3 mL hot water	50 μm CW/TPR	magnetic stirring, 120 min	LD (60 μL methanol: water, 70 : 30, v/v) LC-IT-MS	15–100.2 $\mu\text{g/kg}$	1–60	Blasco et al., 2009
Honey	16 multiclass pesticides	1.5 g honey sample, 10 mL phosphate buffer, homogenization	100 μm PDMS, 85 μm PA	700 rpm, 75 °C, 20 min	TD-GC-M-IPAE	–	20–10000	Campillo et al., 2006
Milk	2 OPPs (coumaphos, dichlorvos)	mixed with buffer solution (HAc and NaAc pH 4.85) (1 : 9, v/v), centrifugation, 16 mL upper layer for SPME	100 μm PDMS	30 °C, 40 min	TD-GC-NPD	0.061–0.511 $\mu\text{g/L}$ (coumaphos)	0.052 (coumaphos) 0.06 (dichlorvos)	Cardeale et al., 2006
Wine	12 multiclass pesticides	filtration, 10 mL sample + 3 g NaCl (30 %, w/v), pH adjusted to 9.5 with 1 mol/L NaOH	60 μm PDMS/DVB	900 rpm, 25 °C, 143 min	LD (1 mL methanol) MEKC-DAD	–	54–113	Ravelo-Pérez et al., 2007
Wine	6 fungicides	–	100 μm PDMS	250 rpm, 60 min	TD-GC-MS/MS	–	(4.4–274)	Kataoka et al., 2009

CE-UV – capillary electrophoresis-ultraviolet detection, CW/TPR – carbowax/templated resins, CNTs-HF – carbon nano tube-reinforced hollow fibre, ECD – electron capture detector, FD – fluorescence detector, FPD – flame photometric detector, GC – gas chromatography, HAc – acetic acid, HPLC-DAD – high performance liquid chromatography- diode array detector, IL – ionic liquid, LC-IT-MS – liquid chromatography-ion trap-mass spectrometry, LD – liquid desorption, LOD – limit of detection, LOQ – limit of quantification, MeCN – acetonitrile, MEKC – micellar electrokinetic chromatography, MIP – molecular imprinted polymer, M-IPAE – microwave-induced plasma atomic emission detector, NaAc – sodium acetate, NPD – nitrogen phosphorus detector, OCPs – organochlorine pesticides, OPPs – organophosphorus pesticides, PA – polyacrylate, PDMS/DVB – poly(dimethylsiloxane)/divinylbenzene, PPy – polypyrrole, QqQ MS – triple-quadrupole MS, SWCNTs – single-walled carbon nanotubes, TD – thermal desorption.

Future trends

In the last years, there has been an increase of interest in microextraction techniques in the field of pesticide residues. Future trends within sample preparation for pesticide residue analysis go through miniaturization and automation and the use of solvent-free techniques, in order to reduce the time required and also decrease the possibility of introducing contaminants (Masiá et al., 2014). SPME can be considered as a well established and widely accepted technique and current research in this field focuses mainly on the development of new coatings and novel analytical strategies that contribute to improvement of sensitivity of the technique (Ramos, 2012). In recent years, additional efforts have been made to improve the SPME

techniques through the development of new fiber coatings and materials through chemical bonding, physical and electrochemical deposition or other methods and introducing ILs, MIPs and CNTs as coating material.

We expect that future research in the testing of new coatings materials will continue. A development of fibers with new extraction phases extend the possibilities of SPME application for selective purposes or may result in the spreading SPME utilization in routine analytical laboratories.

Conclusion

In the last years, there has been an increase in the number of microextraction sample preparation method in the field of pesticide residues in food

Tab. 2. Applicability of solid phase microextraction (SPME) method in head space mode (HS) for the determination of pesticide residues in different food matrices.

Sample	Pesticides	Pretreatment	Fiber	Extraction conditions	Analytical technique	Real samples positive findings	LOD (LOQ) [$\mu\text{g/l}$] [$\mu\text{g/kg}$]	Ref.
Fruit juice (peach, orange, pineapple)	46 multiclass pesticides	1 mL juice	65 μm PDMS/DVB	40 $^{\circ}\text{C}$, 30 min	TD-MDGC-MS	–	–	Ruiz del Castillo et al., 2012
Apple juice, apples, tomato	8 OPPs	juice: dilution in water (1 : 30, w/v), 15 mL diluted sample + 5 g NaCl, apple and tomato homogenization, apple-water dilution (1 : 50), tomato-dilution (1 : 70), 15 mL diluted sample + 5 g NaCl	sol-gel fibres 80 μm B15C5	70 $^{\circ}\text{C}$, 45 min	TD-GC-FPD	tomato 6.35 $\mu\text{g/kg}$ (phorate) 4.9 $\mu\text{g/kg}$ (parathion)	apple juice 0.003–0.075 apple 0.032–0.09 tomato 0.0042–0.076	Cai et al., 2006
Apple	4 pesticides	5 g homogenized sample, dilution with 5 mL deionized water containing 10 % NaCl, ultrasonication for 10 min	100 μm PDMS	60 $^{\circ}\text{C}$, 30 min	TD-GC-MS	0.2 $\mu\text{g/kg}$ (chlorpyrifos)	0.01–0.2	Abdulrauf et al., 2013
Apple	Diphenylamine	cca 2 kg apples placed in three 4.0 L glass jars, sealed and equilibrated for 180 min	100 μm PDMS, PDMS/DVB, PA 7 μm PDMS	30 min	TD-GC-MS		0.72 0.13 0.16 0.61	Song et al., 2014
Fruit and vegetable (strawberry, guava, cucumber, tomato, pakchoi)	8 OPPs, OCPs	chopping, 30 g sample + 30 mL water, homogenization, added 2 % (v/w) methanol:acetone (1 : 1) + 10 % NaCl in distilled water until sample in vial was equal to 5 g	100 μm PDMS	800 rpm, 60 $^{\circ}\text{C}$, 30 min	TD-GC-ECD	6.2–56.8 $\mu\text{g/L}$	0.01–1	Chai et al., 2009
Green apple, strawberries, grape	3 OPPs	30 g sample + 60 mL water, homogenization, sonication, filtration, addition of 1.5 % NaCl (w/v), 1 mL for SPME	100 μm sol-gel hybrid PDMS-2-OHMe18C6	120 rpm, 75 $^{\circ}\text{C}$, 10 min	TD-GC-ECD	–	4.5–4.8	Ibrahim et al., 2010
Fruit and vegetable samples	11 OPPs	1g sample, addition 100 μL methanol/acetone (1 : 1, v/v) +10 % NaCl	100 μm PDMS	70 $^{\circ}\text{C}$, 10 min	GC-MS	lettuce 49 $\mu\text{g/kg}$ (chlorpyrifos)	fruit 0.01–2.7 vegetable 0.17–2.88	Sang et al., 2013
Cucumber, green pepper, Chinese cabbage, eggplant and lettuce	5 OPPs	2 g homogenized sample + 1.2 g NaCl, dilution with 2 mL of distilled water	sol-gel MIP-coated fiber	600 rpm, 70 $^{\circ}\text{C}$, 30min	TD-GC-NPD	without positive findings	0.017–0.77	Wang et al., 2013
Radish	12 OCPs	100 g sample homogenized with 100 mL water, 25 g pyre diluted to 100 mL with water, 4 mL radish matrix solution + 1 g K_2SO_4	100 μm laboratory made fiber with C[4]/OH-TSO	600 rpm, 70 $^{\circ}\text{C}$, 30 min	TD-GC-ECD	–	0.00148–0.174	Dong et al., 2005
Pakchoi	5 OPPs	20 g sample + 60 mL water, homogenization, dilution with water (1 : 20, w/w), 5 mL for SPME	65 μm sol-gel derived OH-TSO/DVB	75 $^{\circ}\text{C}$, 5 min	TD-GC-NPD	–	7–70	Wang et al., 2008

Sample	Pesticides	Pretreatment	Fiber	Extraction conditions	Analytical technique	Real samples positive findings	LOD (LOQ) [$\mu\text{g/l}$] [$\mu\text{g/kg}$]	Ref.
Cow milk	10 OPPs	12 mL for SPME	65 μm PDMS/DVB	600 rpm, 90 $^{\circ}\text{C}$, 45 min	TD-GC-MS	–	2.2–10.9	Rodrigues et al., 2011
Wine	6 OCPs	10 mL sample, addition 10 g/L NaCl	40 μm stainless steel wire coated with PPy-DS film	600 rpm, 70 $^{\circ}\text{C}$, 45 min	TD-GC-ECD	<LOD	0.073–1.659	Korba et al., 2013

2OHMe18C6 – 2-hydroxymethyl-18-crown-6, allyl B15C5 – 3'-allyl benzo-15-crown-5, C[4]/OH-TSO – calix[4]arene/hydroxy-terminated silicone oil, ECD – electron capture detector, GC – gas chromatography, LOD – limit of detection, LOQ – limit of quantification, MDGC-MS – multidimensional gas chromatography-mass spectrometry, MIP – molecular imprinted polymer, NPD – nitrogen phosphorus detector, OH-TSO/DVB – hydroxyl-terminated silicone divinylbenzene, OCPs – organochlorine pesticides, OPPs – organophosphorus pesticides, PA – polyacrylate, PDMS/DVB – poly(dimethylsiloxane)/divinylbenzene, PDMS-2OHMe18C6 – polydimethyl siloxane-2-hydroxymethyl-18-crown-6, PPy-DS – dodecylsulphate-doped polypyrrole, TD – thermal desorption.

matrices. One of them, SPME, have been driven by the move towards the low or none solvent consumption, automatization, sample throughput. In this paper, different fibers, supporting materials, SPME modes and applications of SPME in food analysis were discussed. The most frequently used are commercially available fibres consist of fused-silica fiber as supporting substrate. Moreover, some metallic materials are used as support materials/substrate for SPME fiber. Also, the new laboratory-made fibers prepared on the basis of MIPs, ILs and CNTs have found application in pesticide residue analysis. Sol-gel technology is the most frequently used approach for the preparation of laboratory made fibers in the field of pesticide residues analysis. Higher extraction efficiency for fibers with laboratory-made coating in comparison to commercially available fibers was reported. HS mode was primarily used for determination of OPPs or OCPs in food matrices. Wider application of DI mode in food matrices has been recorded. The pretreatment of the sample prior to SPME is necessary to protect the fiber coating. SPME has been widely used in the analysis of pesticide residues, due to its simple operation and easy coupling to separation techniques (GC, LC) and detection techniques, mainly mass spectrometry. SPME coupled with GC utilizing thermal desorption was the most frequently alternative used. The further development and widespread application of SPME is expected in the future with the advance mainly in the area of new more selective coatings development.

Acknowledgements

This work was supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Academy of Sciences (VEGA, project No. 1/0503/14) and by the Slovak Research and Development Agency under the contract No. APVV-0797-11.

References

- Abdulrauf LB, Tan GH (2013) Food Chem 141: 4344–4348.
- Andraščíková M, Matisová E, Hrouzková S (2015) Sep Purif Rev 44: 1–18.
- Arthur CL, Pawliszyn J (1990) Anal Chem 62: 2145–2148.
- Bagheri H, Es'haghi A, Es'haghi A, Mesbahi N (2012) Anal Chim Acta 740: 36–42.
- Blasco C, Vazquez-Roig P, Onghena M, Masia A, Picó Y (2011) J Chromatogr A 1218: 4892–4901.
- Cai L, Gong S, Chen M, Wu C (2006) Anal Chim Acta 559: 89–96.
- Campillo N, Peñalver R, Aguinaga N, Hernández-Córdoba M (2006) Anal Chim Acta 562: 9–15.
- Capobianco HL, Cardeal ZL (2005) J Braz Chem Soc 16(5): 907–914.
- Cardeal ZL, Paes CMD (2006) J Environ Sci Health Part B 41: 369–375.
- Chai MK, Tan GH (2009) Food Chem 117: 561–567.
- Chowdhury MAZ, Fakhruddin ANM, Islam Md.N, Moniruzzaman M, Gan SH, Alam Md.K (2013) Food Control 34: 457–465.
- Cortés-Aguado S, Sánchez-Morito N, Arrebola FJ, Garrido Frenich A, Vidal JLM (2008) Food Chem 107: 1314–1325.
- Directive 91/414/EEC. Regulation (EC) No 396/2005. Active substances Pesticide EU-MRL. (2005) Off. J. Eur. Union L70: 1.
- Djozan D, Ebrahimi B (2008) Anal Chim Acta 616: 152–159.
- Djozan D, Mahkam M, Ebrahimi B (2009) J Chromatogr A, 1216: 2211–2219.
- Dong C, Zeng Z, Li X (2005) Talanta 66: 721–727.
- Feng J, Qiu H, Liu X, Jiang S (2013) Trends Anal Chem 46: 44–58.
- Filho AM, Neves dos Santos F, Afonso de Paula Pereira P (2008) Talanta 81: 346–354.
- Ghaemi F, Amiri A, Yunus R (2014) Trends Anal Chem 59: 133–143.
- Guillet V, Fave C, Montury M (2009) Journal of Environmental Science and Health Part B 44: 415–422.
- Heaven MW, Nash D (2012) Food Control 27: 214–227.

- Hernández-Borges J, Cifuentes A, García-Montelongo FJ, Rodríguez-Delgado MÁ (2005) Electrophoresis 26: 980–989. http://ec.europa.eu/sanco_pesticides/public/index.cfm.
- Hu Y, Yang X, Wang C, Zhao J, Li W, Wang Z (2008) Food Addit Contam 25(3): 314–319.
- Ibrahim WAW, Farhani H, Sanagi MM, Aboul-Enein HY (2010) J Chromatogr A 1217: 4890–4897.
- Kataoka H, Ishizaki A, Nonaka Y, Saito K (2009) Anal Chim Acta 655: 8–29.
- Korba K, Pelit L, Pelit FO, Özdokur KV, Ertaş H, Eroğlu AE, Ertaş FN (2013) J Chromatogr B 929: 90–96.
- Kudlejova L, and Risticovic S (2012) Application of Solid-Phase Microextraction in Food and Fragrance Analysis. In Handbook of Solid Phase Microextraction: (Ed) Janusz Pawliszyn, Elsevier, Waterloo, Ontario Canada p 291–334. <http://www.sciencedirect.com/science/book/9780124160170>.
- Kudlejova L, Risticovic S, Vuckovic D (2012) Microextraction Method Development. In Handbook of Solid Phase Microextraction (Ed) Janusz Pawliszyn, Elsevier, Waterloo, Ontario Canada, p 201–249. <http://www.sciencedirect.com/science/book/9780124160170>.
- Luo Y-B, Yuan B-F, Yu, Q-W, Feng Y-Q (2012) J Chromatogr A 1268: 9–15.
- Mariani MB, Giannetti V, Testani E, Ceccarelli V (2013) J AOAC Int 96(6): 1430–1434.
- Martins J, Esteves C, Limpo-Faria A, Barros P, Ribeiro N, Simões T, Correia M, Delerue-Matos C (2012) Food Chem 132: 630–636.
- Martins JG, Chávez AA, Waliszewski SM, Cruz AC, Fabila MMG (2013) Chemosphere 92: 233–636.
- Masiá A, Blasco C, Pico Y (2014) Trends Environ Anal Chem 2: 11–24.
- Melo A, Aguiar A, Mansilha C, Pinho O, Ferreira IMPLVO (2012) Food Chem 130: 1090–1097.
- Moliner-Martínez Y, Campíns-Falcó P, Molins-Legua C, Segovia-Martínez L, Seco-Torrecillas A (2009) J Chromatogr A 1216: 6741–6745.
- Munitz MS, Resnik SL, Montti MIT (2013) Food Chem 136: 1399–1404.
- Pereira VL, Fernandes JO, Cunha SC (2014) Trends Food Sci & Technol 36: 96–136.
- Ramos L (2012) J Chromatogr A, 1221: 84–98.
- Ravelo-Pérez LM, Hernández-Borges J, Borges-Miquel TM, Rodríguez-Delgado MÁ (2007) Electrophoresis 28: 4072–4081.
- Rodrigues FM, Mesquita PRR, Oliveira LS, Oliveira FS, Filho AM, Pereira PAP, Andrade JB (2011) Microchem J 98: 56–61.
- Ruiz del Castillo ML, Rodriguez-Valenciano M, Peña Moreno F, Blanch GP (2012) Talanta 89: 77–83.
- Sagratini G, Mañes J, Giardiña D, Damiani P, Picó Y (2007) J Chromatogr A 1147: 135–143.
- Sang Z-Y, Wang Y-T, Tsoi Y-K, Leung KS-Y (2013) Food Chem 136: 710–717.
- Sapahin HA, Makahleh A, Saad B (2015) Arabian Journal of Chemistry <http://dx.doi.org/10.1016/j.arabjc.2014.12.001>.
- Saraji M, Rezaei B, Boroujeni MK, Bidgoli AAH (2013) J Chromatogr A 1279: 20–26.
- Song J, Forney CF, Jordan MA (2014) Food Chem 160: 255–259.
- Song X-Y, Shi Y-P, Chen J (2013) Food Chem 139: 246–252.
- Souza-Silva ÉA, Lopez-Avila V, Pawliszyn J (2013) J Chromatogr A 1313: 139–146.
- Tian M, Cheng R, Ye J, Liu X, Jia Q (2014) Food Chem 145: 28–33.
- Tranchida PQ, Zoccali M, Schipilliti L, Sciarrone D, Dugo P, Mondello L (2013) J Sep Sci 36: 2145–2150.
- Viñas P, Campillo N, Martínez-Castillo N, Hernández-Córdoba M (2009) J Chromatogr A 1216: 140–146.
- Wang Y-L, Gao Y-L, Wang P-P, Shang H, Pan S-Y, Li X-J (2013) Talanta 115: 920–927.
- Wang Y-L, Zeng Z-R, Liu M-M, Yang M, Dong C-Z (2008) Eur Food Res Technol 226: 1091–1098.
- Wu F, Lu W, Chen J, Liu W, Zhang L (2010) Talanta 82: 1038–1043.
- Yang C, Wang J, Li D (2013) Anal Chim Acta 799: 8–22.
- Zhao GY, Wang C, Wu QH, Wang Z (2011) Analytical Method 3: 1410–1417.