Chapter 2
PROTOCOLS FOR EXTRACTION OF PESTICIDE RESIDUES

María Luisa Fernández de Córdova[1] **and Eulogio José Llorent Martínez**

Contents

---

[1] M.L. Fernández de Córdova (corresponding author)

Department of Physical and Analytical Chemistry, Faculty of Experimental Sciences, University of Jaén, Campus Las Lagunillas s/n, E-23071, Jaén, Spain. ORCID iD: 0000-0002-4500-4246.

E.J. Llorent Martínez

Department of Physical and Analytical Chemistry, Faculty of Experimental Sciences, University of Jaén, Campus Las Lagunillas s/n, E-23071, Jaén, Spain. ORCID iD: 0000-0002-0180-5172.

Abstract. Over the past few years, the presence of pesticides in foods has received growing attention as one of the main food safety problems. Many countries and health organizations have dictated increasingly stringent regulations on the maximum residue limits for pesticides in foodstuffs, which are based on sensitive and trustworthy methods for pesticide residue analysis. Pesticides can also reach surface water through runoff from treated plants and soil, contaminate groundwater, soil, ground and grass and be toxic to non-target organisms. Therefore, it is necessary to develop highly selective methods of analysis that can ensure accurate and precise results with sufficiently low detection limits for a wide range of pesticides. Due to the large number of pesticides on the current market, multiclass and multiresidue methods are certainly the best way to address the problem of pesticide analysis and, in recent years, the general tendency has been the development of increasingly sensitive, accurate, precise and rapid methods.

Despite the enormous progress made in the development of highly efficient analytical instrumentation for pesticide determination in samples of a very different nature, in most cases a pretreatment of the sample is still required to extract, isolate and concentrate the target compounds since it is generally not possible to directly manipulate the sample. Sample preparation often includes a cleanup step in order to remove non-specific matrix co-extractives, especially for analysis of very complex matrices such as foodstuffs and environmental samples, which also brings the analytes to an appropriate concentration level. Conventional sample treatment techniques are efficient, but they entail drawbacks such as the employ of toxic organic solvents that cause environmental contamination and additional operational costs for waste treatment, complicated procedures that require a lot of time, and difficulty in automation. Therefore, in recent years a lot of techniques have been developed in order to miniaturize and simplify the sample treatment, and reduce the amount of organic solvents used for meeting the requirements of green chemistry. Nevertheless, the pesticide residue analysis is an ongoing challenge mainly due to low concentration of pesticides, as well as the large quantities of compounds in the matrix that can be co-extracted, often giving rise to errors and damage to analytical instrumentation. In this chapter, the main classical and advanced methodologies available for the treatment of food and environmental samples for analysis of pesticide residues are summarized and explained. These techniques include: liquid-liquid extraction, Soxhlet extraction, supercritical fluid extraction, microwave-assisted extraction, pressurized liquid extraction, gel permeation chromatography, solid-phase extraction, matrix solid-phase dispersion, solid-phase microextraction, QuEChERS, stir bar sorptive extraction, and liquid-phase microextraction. Their advantages, drawbacks and future perspectives are also discussed.

Keywords: pesticides · extraction · cleanup · sample preparation · microextraction techniques · liquid-phase extraction techniques · solid-phase extraction techniques · food samples · environmental samples · green analytical chemistry

2.1 Introduction

In recent years, the application of pesticides has rapidly increased mainly in agriculture thus their use allows having abundant and high quality vegetables available at a relatively low price. However, the presence of pesticide residues in foods, soils, plants and water has become a major issue and could have considerable impact on health and the environment (Samsidar et al. 2018). To ensure that pesticide residues found in foods do not represent an unacceptable risk for human consumption, most governments have set maximum residue limits in vegetables and fruits. Maximum residue limits of pesticides in food and feed are internationally restricted by the Regulations of the European Union and Codex Alimentarius Commissions (European Union 2005; Codex Alimentarius: http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/en/), which reflect the highest amount of residues expected in food when plant protection products are applied correctly in accordance with authorized conditions of use. They are not safety limits, and are always set below, often far below, levels that would present a risk to consumers. The European Union maximum residue limits apply to most food commodities of animal and plant origin, concretely to the product as placed on the market. In the last European Union report on pesticide residues in foods, which provides an insight into the official control activities carried out by European Union Member States, Iceland and Norway in 2016, pesticide concentrations in 96.2% of the 84,657 samples analyzed met the established legal limits. Similar to the results obtained in 2015, processed grape leaves, rice, wild fungi, tomatoes, sweet peppers, sweet corn, table grapes, and table olives were the commodities that most frequently exceeded the maximum residue limits. Teas, strawberries, pineapples, milk (goat) and muscle (swine) were also found to exceed frequently the maximum residue limits (more than 2% of the samples) (European Food Safety Authority 2018). On the other hand, in the European Union pesticide residues in water are subject to the Water Framework Directive, whose purpose is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater (European Union 2000). In accordance with the above, it is very important to provide accurate, precise and reliable methods for pesticide residue analysis for ensuring food safety and preserve environment.

Currently, the determination of pesticides has received more attention because governments have reduced the maximum residue limits, and hence the detection of trace levels of pesticides needs more efficient techniques for pre-treatment of samples. The analytical procedure usually consists of numerous stages, being the sample collection and its preparation for analysis the most important ones. Sample preparation is often a neglected area even though it plays an essential role in the whole analytical procedure, particularly in the analysis of solid samples. Most analytical instruments are unable to handle matrices directly and, therefore, some form of sample pretreatment is required to extract and enrich analytes. Environmental and food samples are complex and very diverse and analytes are usually found at trace and ultra-trace amounts (Stocka et al. 2011) so that sample preparation has a special relevance. From an analytical point of view, a sample pretreatment for pesticide residue analysis should to have the following features: (a) to allow the analysis of a number of pesticides as large as possible in a single run (multiresidue method); (b) to provide recovery percentages as close as possible to 100%; (c) efficient removal of potential interfering species from the matrix; (d) high sensitivity; (e) good precision; (f) good ruggedness; (g) low cost; and (h) high throughput. Moreover, sample treatment should be environmentally friendly so that it implies the use of as low solvent volumes as possible (Hercegová et al. 2007).

Typical sample preparation for pesticide analysis includes the following steps: sampling/homogenization, extraction of target compounds from the bulk of the matrix, and cleanup of analytes from matrix co-extractives. Among them, the extraction of the target compounds and cleanup of the extracts are the most time-consuming and challenging steps and play a key role in the success of analysis. Special attention must be paid to high-fat content matrices, since it is necessary to avoid high amounts of fat residues in the final extracts, which would affect to the proper functioning of the chromatographic system. Although conventional methods of extraction, especially liquid-liquid extraction, have been widely used for analysis of pesticide residues, they are subject to the loss of pesticides due to the long and laborious experimental procedure, require large amounts of organic solvents, and are time-consuming. Therefore, over the past years analytical developments have attempted to minimize the solvent volumes, the use of toxic solvents, the physical and chemical manipulations, and have aimed to automate the extraction and cleanup procedures as far as possible (LeDoux 2011). Figure 1 shows the desired analytical characteristics and current trends in the treatment of samples for pesticide residue analysis.

Figure 1

To date, a lot of techniques have been exploited for determination of pesticide residues. Following the extraction/cleanup steps, the detection of pesticides is usually performed by mass spectrometric techniques (i.e. tandem mass spectrometry using ion-trap or triple quadrupole instruments) in combination with gas chromatography or liquid chromatography, owing to their high sensitivity, selectivity and throughput. Most of the traditional methods for analysis of pesticide residues have been applied to the determination of a single component or a class of pesticides. On the contrary, multiresidue methods of analysis are used for analysis not only of several components of the same class of pesticides, but also of several components of different classes of pesticides. Taking into account the large number of pesticides on the market, the development of multiresidue methods capable of analyzing large number of pesticides in one single run is the most efficient and common approach. These multiresidue methodologies, in addition to allow the determination of a large number of compounds in one run, should provide large recoveries of target compounds, high sensitivity and good precision, ensure maximum removal of interfering species from extracts, and be environmentally-friendly, quick, cheap and easy to carry out.

Many works have been reported over the years to achieve this objective. The present chapter describes a review of the main techniques used for extraction and cleanup in field of pesticide residue analysis. The basic principles and main features of both classical and modern techniques are described, compared their advantages and disadvantages, and their ability and applicability for pesticide residue analysis. A distinction has not been made between techniques for extraction and purification since in practice most of them are used for both purposes. After introducing these techniques and their applications, particular attention will be paid on the recent developments and future trends. The main focus has been paid on microextraction techniques, since currently they constitute one of the main trends in the development and enhancement of sample treatment methods. Finally, the applications addressed in the present chapter cover food samples and aqueous and solid environmental samples.

2.2 Liquid-phase extraction techniques

2.2.1 Liquid-liquid extraction

Liquid-liquid extraction, also called solvent partitioning, is a conventional technique used for sample preparation and preconcentration. The extraction of the organic compounds is based on their relative solubilities in two immiscible liquids, water and an organic solvent or two organic solvents. The factors influencing efficiency of the extraction are: solubility of the compounds in the extraction solvent, extraction volume and number of extractions. In the conventional extraction of organic compounds the solid or liquid sample is homogenized and repeatedly extracted with an organic solvent; then, the extracts are centrifuged, concentrated and/or purified to remove matrix co-extractives before the final analysis. The techniques used for cleanup of the extracts usually are gel permeation chromatography and/or solid-phase extraction (Guardia-Rubio et al. 2006; Zheng et al. 2014). This is an efficient extraction technique in terms of recovery, except for a few pesticides such as hexachlorobenzene for instance which is very volatile (LeDoux 2011). In this technique solvents or solvent mixtures are used for extraction, according to the polarity of target compounds. In the development of multiresidue methods it is necessary to take into account that the solvents used have to be able to extract pesticides with a wide range of polarities from the same matrix. Moreover, pesticides can be accompanied by their metabolites or degradation products, whose extraction requires different solvent systems according to their polarity.

The usual solvents for liquid-liquid extraction of pesticides in food and environmental matrices have been ethyl acetate (Fernandez-Alba et al. 1994; Mol et al. 2007; Banerjee et al. 2007), acetone (Guan et al. 2010), methanol (Hanot et al. 2015), hexane (Cabras et al. 2001), dichlorometane and acetonitrile (Fillion et al. 2000; Lehotay et al. 2001; Guardia Rubio et al. 2007). Mixtures of these solvents with different composition have also been widely used, such as hexane/dichloromethane (Tian et al. 2019), hexane/acetone (Rezić et al. 2005), hexane/acetonitrile (Zayats et al. 2013), or dichlorometane/acetone (Pose-Juan et al. 2006). The use of medium polarity solvents such as ethyl acetate or acetone can increase the polarity of a non-polar solvent or decrease the polarity of a polar solvent in the extraction procedure. Acetone is completely miscible with water and allows an adequate penetration in the aqueous part of the sample. However, to induce its separation from the water phase a non-polar solvent has to be added, which leads to dilution and can originate low recoveries of the most polar analytes. Ethyl acetate is sufficiently miscible with water to allow good penetration into matrices and its polarity is sufficient to extract the most polar pesticides. Moreover, after extraction no extra partition step is required, since water can be simply removed by adding sodium sulfate. Acetonitrile is miscible with water, but it can be separated from the aqueous phase by salting-out effect. In addition, due to its hydrophobicity, it is efficient in extracting both polar and non-polar pesticide residues with low amounts of matrix co-extractives. Therefore, acetonitrile has been one of the most widely used solvents for liquid-liquid extraction of pesticide residues. Acetonitrile also presents an additional advantage, the possibility to analyze in the same extract both gas chromatography- and liquid chromatography-amenable analytes (Anastassiades et al. 2003; Lehotay et al. 2005a), since it is compatible with reversed-phase liquid chromatography and can also be served as a medium for gas chromatography injection. As a rule, less polar organic solvents such as dichlorometane or hexane favor extraction of more non-polar pesticides and can be occasionally used for the extraction of non-polar pesticides or to modify the polarity of other non-polar solvents (Zhang et al. 2014).

Classical liquid-liquid extraction is aided by shaking, but ultrasonic extraction has also been widely applied for extraction of pesticides from solid food and environmental samples (Gonçalves and Alpendurada 2005; Lambropoulou et al. 2006). Acoustic energy is used for enhancing mechanical washing of the sample, providing a high efficient contact between sample matrix and solvent. Several studies show that ultrasonic extraction is an effective technique during sample preparation for pesticide analysis in soil, sediments, oil, coffee, honey and fruits and leafy vegetables (Beyer and Biziuk 2008; Pan et al. 2008; Da Silva Souza and Navickiene 2019; Tian et al. 2019). Moreover, it was reported that ultrasonic extraction can allow excellent results without cleanup if solvent type and extraction conditions are optimized (Rezić et al. 2005).

Conventional liquid-liquid extraction is an accepted and popular technique for sample preparation due to its advantages like simplicity, efficiency, and ruggedness. This technique mostly provides recovery percentages for pesticide residue analysis in the range 70-120%, as advised by the European Union. Multiresidue methods also show recoveries in this range for over 80% of the analytes (LeDoux 2011). However, liquid-liquid extraction presents many inherent drawbacks, e.g., it requires a relatively large amount of matrix, and the evaporation of a large quantity of toxic and flammable solvents to get to required pre-concentration coefficient. Moreover, it is time-consuming, laborious, expensive regarding the consumption of solvents and other materials, and difficult to automate. These drawbacks have been overcome by the introduction of simpler and faster sample preparation methods for pesticide residue analysis in foods and environmental samples. The advent of novel modified liquid-liquid extraction methods in the sample treatment field has caused the decrease of organic solvent consumption, more effective extraction, higher extraction yields and on-line connecting to analytical instrumentation. These techniques are described in the next Sections.

2.2.2 Soxhlet extraction

Conventional Soxhlet has been used for decades as one of the most relevant techniques in the environmental pesticide extraction field from solid samples. In this technique, a glass extractor consisting of three parts is used: a distillation flask, a main chamber and a coolant. The sample is placed inside a thimble-holder and deposited in the main chamber, covering it with the extraction solvent. The solvent is then heated to reflux so that its vapors condense into the coolant and drop down on the sample cartridge. When the liquid in the central chamber reaches an overflow level, it passes through a siphon to the distillation flask by dragging with it the compounds extracted from the sample. This operation is repeated until the extraction is completed. Therefore, this performance makes Soxhlet a hybrid discontinuous-continuous technique. Soxhlet extraction has been mostly applied to the extraction of organochlorine pesticides from different matrices, such as soils (Wang et al. 2007b), river sediments (Tan and Vijayaletchumy 1994), fatty foods (Doong and Lee 1999), mollusks and crabs (Yang et al. 2006), and eggs, chicken and meat (Ahmad et al. 2010). The solvents used usually are either *n*-hexane or *n*-hexane/acetone, although other solvents such as acetone/dichlorometane or ethyl acetate have also been reported (Luque de Castro and Priego-Capote 2010). In the application of Soxhlet for the extraction of pesticides from soils, it is necessary to take into account that the strong organic solvents used are not able to solubilize humate matter, which may contain pesticides with a high affinity to organic humic acids, such as organochlorine pesticides (Andreu and Picó 2004).

Soxhlet extraction integrates the advantages of the reflux extraction and percolation, which uses the principle of reflux and siphoning to continuously extract samples with fresh solvent. It provides high extraction efficiency and requires less time and solvent consumption than maceration or percolation. The most significant drawbacks of Soxhlet are: large amounts of solvent usage (300-500 mL per sample), the need for evaporation solvent to concentrate analytes before analysis, it is expensive in terms of energy, cleanup of extracts is usually needed, and long extraction times are required (e.g. up to 24-48 h). In addition, this technique cannot be used for thermolabile compounds such as *N*-methylcarbamates, sulfonyl urea, and chlorophenoxy acid herbicides, since prolonged heating may lead to their degradation.

2.2.3 Microwave-assisted extraction

Microwave-assisted extraction has been demonstrated to be a versatile extraction technique for pesticide residue analysis in solid samples, with the advantages of rapidity, simplicity and low cost of operation (Hercegová et al. 2007; Merdassa et al. 2013). This technique has also been successfully applied to the extraction of liquid samples (Fuentes et al. 2009). Microwave energy is a non-ionizing radiation (frequency 300–300000 MHz), which can get in certain materials to interact with the polar components by ionic conduction and rotation of dipoles, and generate heat (Sparr Eskilsson and Björklund 2000). No drying of sample is required since water absorbs microwave energy quickly and can help to heat up sample. The most common procedure in microwave-assisted extraction involves extraction in a closed vessel under controlled temperature and pressure, although a focused microwave oven at atmospheric pressure is also used (Falqui-Cao et al. 2001; Fuentes et al. 2009).

When compared to conventional heating, microwave-assisted extraction presents advantages such a significant decreasing of time of analysis because the heat is transferred directly to the solvent, and an easy control of extraction parameters (temperature, power, time). Moreover, thermolabile compounds can be extracted by appropriately controlling working conditions and trace analytes can be extracted from very low amounts of sample. However, microwave-assisted extraction has several drawbacks such as: partial decomposition of some compounds in high pressure and temperature conditions can occur; volatile compounds can be lost at the end of the process, so that the vessels must be cooled at room temperature before being opened; extracts must be filtered after extraction; polar solvents are necessary; and cleanup of extracts is usually needed since microwave-assisted extraction is very efficient.

Some of these drawbacks can be overcome when this technique is carried out in on-line mode by coupling the instrument to a flow system consisting of a high-pressure quaternary gradient pump for solvent delivery (Carvalho et al. 2008). In this modality of microwave-assisted extraction the extract can be on-line filtered and subjected to other coupled subsequent pre-treatments. The degradation of thermolabile compounds can be avoided by using dynamic mode. In dynamic microwave-assisted extraction fresh solvent is continuously pumped through the extraction vessel and analytes are transferred out of the vessel as soon as they are extracted (Wang et al. 2012a; Wu et al. 2016).

The choice of an appropriate solvent in microwave-assisted extraction is essential for getting an optimal extraction yield. The pesticide extraction process may occur through two different heating mechanisms (Sparr Eskilsson and Björklund 2000): immersion of sample in a high dielectric constant solvent or mixture of solvents that absorb microwave energy efficiently (Font et al. 1998); and immersion of sample in a combination of low and high dielectric constant solvents (Chee et al. 1996).

In recent years, there has been a general interest for the development of microwave-assisted extraction methods based on the use of extraction media alternative to toxic organic solvents, such as micellar (surfactant-rich) systems (Moreno et al. 2007) or ionic liquids (Wang et al. 2013). Ionic liquids are liquid salts with melting points close to or below room temperature, which act as surfactants and absorb microwave radiation extremely well and transfer energy quickly by ionic conduction to the matrix, thus improving extraction efficiency and speed of analysis. Aqueous solutions or steam have also been used as green solvents to extract pesticides from solid samples. Song et al. (2014) developed an on-line and green microwave-assisted extraction approach to extract carbamate pesticides in rice with water steam. The extract was subjected to an additional cleanup and concentration step by solid-phase extraction on a octadecylsilane cartridge. Recoveries ranging from 66% to 117% were obtained with relative standard deviation values below 9.1% for all the pesticides. Limits of detection of 1.1–4.2 ng g^{-1} were achieved by liquid chromatography-tandem mass spectrometry analysis.

2.2.4 Pressurized liquid extraction

Pressurized liquid extraction, also known as accelerated solvent extraction, is a well-known technique in the field of pesticide residue analysis that involves the extraction of residues from solid or semi-solid samples (Vazquez-Roig and Picó 2015; Khan et al. 2018; Andreu and Picó 2019). In this technique the extraction is carried out with small amounts of water and organic solvents (15-40 mL) at high temperatures (up to 200 ºC) and pressures (up to 3000 psi) for short time periods, which results in better extraction efficiency and reduction of solvent volume compared with traditional extraction techniques such as liquid-liquid and Soxhlet extraction. Sample (5-100 g) is usually dried to enhance the solvent penetration into the matrix, mixed with a solid sorbent (e.g., Hydromatrix, diatomaceous earth, or sea sand) that reduces particle clumping and solvent channeling in the extraction process, and loaded into the stainless-steel closed-cell (Juan-García et al. 2010; Choi et al. 2016). Pressurized liquid extraction is usually carried out in static mode, although it can also be operated in dynamic mode by continuously pumping small volumes of solvent through the extraction cell at a specified flow rate (0.5–2.5 mL min^{-1}), which accelerates the mass-transfer rate (Vazquez-Roig and Picó 2015). The extraction time of both modes is usually similar and the extraction efficiency of dynamic mode is equal or even higher than when using static mode. The drawback of dynamic mode is that it requires a larger volume of fluid than the static mode, so that analytes will be diluted in the extract, and a pre-concentration step will be required before their chromatographic analysis.

The majority of instruments allow loading up to 24 cells, no filtration is required, and the extraction can be done in unattended operation. Elevated temperature breaks matrix-analyte interactions and achieves a higher diffusion rate, improving the solubility of the analytes in the extraction solvent. On the other hand, elevated pressure raises the solvent to the near-supercritical region, where it shows better extraction properties. Moreover, at high temperature and pressure, viscosity and surface tension of solvent decrease, so that it penetrates into solid sample pores more efficiently (Beyer and Biziuk 2008; Vazquez-Roig and Picó 2015). Extraction time hardly depends on the sample amount, whereas extraction efficiency principally depends on temperature. During the development of a pressurized liquid extraction method it is necessary to optimize several parameters, including extraction time and temperature, type of solvent and sorbent, and number of extraction cycles. Although high temperatures increase extraction efficiency, they may cause the degradation of thermolabile compounds, and also increase the amount of matrix co-extractives. Thus, in the case of fatty matrices, the presence of large amounts of co-extracted lipids constitutes a major problem, and a further cleanup of the extract is usually required (Choi et al. 2016). Therefore, it will be necessary to make a compromise between achieving maximum extraction efficiency and minimizing the amount of co-extractive species. Solvents used for extraction of pesticide residues include hexane (Pinto et al. 2014), acetone (Moreno-González and León 2017), ethyl acetate (Khan et al. 2018), acetonitrile (Masiá et al. 2015), and water (Juan-García et al. 2010). Mixtures of solvents such as hexane-dichlorometane (Choi et al. 2016), acetonitrile-water (Homazava et al. 2014), acetone-dichlorometane (You et al. 2010; Köck-Schulmeyer et al. 2013; Clark et al. 2015), and hexane-acetone (Celeiro et al. 2014) have also been used.

The small volumes of extracts facilitate further concentration and cleanup, usually performed by solid-phase extraction (You et al. 2010; Wang et al. 2010; Köck-Schulmeyer et al. 2013). Fairly recently, a new approach, called selective pressurized liquid extraction, that combines extraction and '*in-cell*' cleanup step, has been reported. Several sorbents placed at the bottom of the pressurized liquid extraction cell are used for cleanup of the extracts, so that the need for additional manipulation of sample is avoided (Homazava et al. 2014; Pinto et al. 2014; Masiá et al. 2015). Choi et al. (2016) studied which sorbent was better for '*in-cell*' cleanup in the extraction of organochlorine pesticides in fish. The efficiency in the removal of lipids in decreasing order was: Alumina > acid-treated silica gel > alumina and acid-treated silica gel > Florisil > alumina and silica gel.

Pressurized liquid extraction is mostly combined with liquid chromatography or gas chromatography for analysis of pesticide residues, coupled with both low and high resolution mass spectrometry (Andreu and Picó 2019), although capillary electrophoresis has also been used (Juan-García et al. 2010). Currently, pressurized liquid extraction is already a routine technique for trace analysis of pesticides and other organic contaminants, used in many laboratories because of its short extraction time, easy manipulation, low sample-amount requirements and good performance. However, it requires sophisticated and expensive equipment and higher consumption of energy than other traditional extraction techniques.

2.2.5 Supercritical fluid extraction

Supercritical fluid extraction is usually an efficient technique, mainly applicable to solid samples. Fluids are defined as supercritical when they are maintained at pressures and temperatures above the critical point. Supercritical fluids densities are greater than those of gases and close to those of liquids and, consequently, their solvation properties are similar to those of liquid solvents. Moreover, they have lower viscosity than traditional liquid solvents, which increases the diffusion of solutes in the solvent. CO_2 is most widely used as a supercritical fluid because of it is a nonflammable, nontoxic, and environmentally-friendly solvent. Supercritical fluid extraction does not use hazardous solvents and is easily automated, so reducing the time, cost and manual labor required for extraction. Furthermore, selectivity of extraction can be easily controlled by varying the density of the supercritical fluid, which depends on pressure and temperature. Taking into account that the supercritical CO_2 fluid has low polarity, at a constant temperature, it will be capable to extract low polar analytes at low pressure, and very polar analytes at high pressure (Zougagh et al. 2004). Supercritical fluid extraction is usually carried out at pressures that are not high enough to efficiently extract polar analytes. Therefore, in supercritical fluid extraction, the range of analytes that can be extracted with CO_2 is limited due to its low polarity, being considered a nonpolar solvent with a liquid solubility equal to that of hexane. To overcome this problem, polar solvents (modifiers or co-solvents) are often added to modify the CO_2 fluid or sample matrices for optimal extraction of polar pesticides. The modifier can influence the extraction process in three ways, which depends on the type of sample matrix and the analyte's retaining nature on the matrix: (a) increasing the solubility of the analyte in the supercritical fluid, because of the interaction modifier-analyte in the fluid phase; (b) competing with the analytes for the active sites in the matrix, so facilitating the desorption of the analyte; (3) distorting the matrix, which favors the penetration of the supercritical fluid inside the matrix. Nemoto et al. (1997) showed that water and alcohols were effective modifiers for improving the recovery of pesticides. Methanol is the most common solvent added to CO_2 although other solvents such as acetonitrile (Rissato et al. 2004) have also been used.

The application of supercritical fluid extraction to pesticide residue analysis has been demonstrated for some pesticides in samples such as sediments (Janda et al. 1989), soil (Rissato et al. 2005), oils (Hopper 1999), and agricultural products (Howard et al. 1993; Valverde-García et al. 1995). Nevertheless, supercritical fluid extraction technique has not been widely used for pesticide residue analysis in foods of animal origin since, in the first attempts carried out in these matrices, the recoveries obtained were unacceptable for many pesticides. However, other authors as Fiddler et al. (1999) reported very good recoveries in matrices such as eggs, ranged from 81.8 to 108.3%. Several applications of supercritical fluid extraction to multiresidue analysis of pesticides have also been reported (Lehotay and Eller 1995; Snyder et al. 1993). The most recent studies have shown than supercritical fluid extraction methods combined with an additional cleanup step by solid-phase extraction (Norman and Panton 2001; Rissato et al. 2005; Ono et al. 2006) or QuEChERs (Sartori et al. 2017) meet the strict criteria established for the analysis of pesticide residues.

Large scale supercritical fluid extraction can compete economically with traditional extraction and separation processes, but at the laboratory scale it has serious disadvantages such as high equipment and upkeep cost, difficult optimization, and high blank and noise values (LeDoux 2011).

2.2.6 Liquid-phase microextraction techniques

To overcome the drawbacks of conventional liquid-liquid extraction and provide fast, simple and green procedures, several liquid-phase microextraction techniques by reducing organic solvent consumption and simplifying sample preparation procedures have been developed. These techniques are the result of the miniaturization of conventional liquid-liquid extraction by greatly reducing the solvent volume to just a few microliters, and they combine in one step extraction, concentration, and sample introduction. As consequence of the small volume of solvent used for extraction, in liquid-phase microextraction techniques almost all of the obtained organic extract can be injected into the separation instruments, unlike in liquid-liquid extraction where only part of the extract is injected (Lambropoulou and Albanis 2007). In liquid-phase microextraction the extraction is performed between an aqueous phase containing the analytes (donor phase) and a small volume of water-immiscible solvent (acceptor phase) (Sarafraz-Yazdi and Amiri 2010). Two modes of working are possible: to immerse directly the acceptor phase in the sample solution or hang it above the sample for headspace extraction. Most methods reported for the liquid-phase microextraction of pesticides focus on liquid samples, although several applications of liquid-phase microextraction to solid matrices have also been developed. These latter are usually based on the combined use of liquid-phase microextraction with a previous treatment that implies a conventional extraction with organic solvent or another extraction technique such as microwave-assisted extraction (Basheer et al. 2005), ultrasonic extraction or pressurized liquid extraction (Lüthje et al. 2005). However, liquid-phase microextraction has also been applied to the direct extraction of pesticide residues in solid samples such as vegetables (Romero-González et al. 2006) or soils (Hou and Lee 2004) without a previous treatment of sample.

Three major categories of liquid-phase microextraction techniques have been developed to date, which differ in the way in which sample and extraction solvent are contacted: a) single-drop microextraction; b) hollow-fiber microextraction; and c) dispersive liquid–liquid microextraction. All them will be review from here on out.

2.2.6.1 Single-drop microextraction

In single-drop microextraction the extraction phase is a micro-drop of organic solvent, so that analyte extraction and preconcentration take place in a single run. The extraction is assisted by stirring, so that the surface of the drop is continuously exposed to fresh aqueous sample and the thickness of the static layer is reduced, which enhances extraction efficiency. A relevant feature of single-drop microextraction is that the drops generated can be renewed for each extraction, so that there is no sample carryover. After extraction, the micro-drop is withdrawn back into the syringe and usually transferred to a gas chromatography or liquid chromatography instrument for further analysis. Single-drop microextraction, of all the solvent microextraction techniques, is also the most easily fully automated method developed to date (Kokosa 2015), and it has been widely applied to analysis of pesticide residues in foods and environmental samples containing target compounds in trace amounts (Zhao et al. 2006; Xiao et al. 2006; Tian et al. 2014).

In practice, single-drop microextraction can be performed by two main approaches (Figure 2):

(1) direct immersion
(2) headspace

Figure 2

In direct immersion single-drop microextraction, a droplet of a water-immiscible solvent hangs from the tip of a syringe needle immersed in an aqueous sample. Applications of direct immersion single-drop microextraction are usually limited to nonpolar and medium polarity analytes, since the organic solvents used have to be immiscible with water (Zhao et al. 2006; Sarafraz-Yazdi and Amiri 2010; Garbi et al. 2010; Pano-Farias et al. 2017). Two important drawbacks of direct immersion single-drop microextraction are the limited size (typically 1-3 μL) and instability of the droplet when fast stirring is used. A number of recent advances in this technique have focused to overcome these problems, such as the use of support materials to stabilize the extraction solvent and adaptors for the normal syringe needle (Kokosa 2015). One of the strategies developed is the use of bubble-in-drop technique, which consists in the incorporation of a constant volume of air into the solvent drop (Williams et al. 2011). The solvent is drawn into a microsyringe, followed by air, and when the syringe is depressed to expel the contents into the sample solution, a bubble of solvent containing an air bubble is produced at the tip. As long as the solvent is immiscible in the sample solution, it will remain at the end of the tip until it is drawn back into the syringe. For solvents denser than water, the bubble incorporated into the drop stabilizes it due to its buoyancy, making it less likely to fall from the needle. Moreover, the surface area of the drop is increased, which enhances the extraction efficiency. This methodology was used for the analysis of metolochlor and atrazine herbicides using gas chromatography-mass spectrometry. A 0.5 μL air bubble in a 1 μL volume of chloroform was used for the extraction procedure. The results gave limits of detection from 0.024 ng L^{-1} for atrazine to 0.013 ng L^{-1} for metolochlor (Williams et al. 2014).

In headspace single-drop microextraction, volatile compounds are extracted by placing the drop of solvent generated in a microsyringe in the headspace of the sample solution or a flowing air sample stream. Therefore, the use of water and water-miscible solvents is possible in this mode of single-drop microextraction, which significantly increases the range of both extractable analytes and analytical methods that can be coupled to headspace single-drop microextraction. Moreover, in headspace single-drop microextraction technique a very efficient cleanup of the sample is carried, so that it is a suitable extraction technique for complex matrices. Salemi et al. (2013) successfully applied this technique for extraction of organophosphorus pesticides from soil and compared the results obtained with those provided by using direct immersion single-drop microextraction. According to the authors, direct contact of the extraction phase with the sample would lead to at least three main drawbacks: increasing risk of solvent droplet contamination with interfering non-volatile sample components and also solid particles; decreasing of stability of the solvent drop; and limitation in the range of some experimental parameters, such as agitation power or speed, water/soil ratio and modifying solvent due to the presence of the solvent drop in the sample phase. The limits of detection achieved ranged from 0.1 to 2.0 ng g^{-1} and the method was also reproducible with relative standard deviations of 2.1–6.9%.

Originally, relatively low-viscosity/low-boiling organic solvents, such as toluene, chloroform, cyclohexane, and 1-octanol, were used in single-drop microextraction because of being compatible with gas chromatography. Solvent volatility resulted in the evaporation of the drop, especially when elevated extraction temperatures were used. Later, the replacement of organic solvents for microextraction of organic compounds by ionic liquids, ionic media containing organic and inorganic anions coupled with organic cations, was proposed. These solvents have high viscosity and high boiling point, which reduces evaporation, allows the use of larger and more reproducible extraction volumes, and allows long-time headspace extraction even at high temperature (Liu et al. 2003). Moreover, ionic liquids can be considered as '*green*' solvents and are easily synthesized or commercially available. Headspace single-drop microextraction employing ionic liquids as extraction solvents has been successfully used for extracting pesticides. 1-butyl-3-methylimidazolium hexafluorophosphate ([C4MIM][PF6]) was employed as an extraction solvent for the analysis of dichlorodiphenyltrichloroethane (*p,p'*-DDT and *o,p'*-DDT) and its metabolites in water samples by high-performance liquid chromatography with ultraviolet detection (Ye et al. 2006). Zhang and Lee (2010) also developed a headspace single-drop microextraction method using the same ionic liquid for extraction, followed by gas chromatography with electron capture detection, which was applied to the analysis of organochlorine pesticides in soils.

Recently, single-drop microextraction has emerged as one of the simplest and most easily implemented forms of micro-scale sample pre-concentration and cleanup for pesticide analysis because it provides high selectivity, good quantitation, low limits of detection, no carryover, and minimal sample preparation.

2.2.6.2 Hollow-fiber microextraction

Pedersen-Bjergaard and Rasmussen (1999) introduced an innovative alternative to single-drop microextraction with the aim of improving the reliability of this technique and avoid one of its main shortcomings, instability of the extracting phase. They proposed to use a porous polypropylene hollow-fiber membrane as a support for the extraction solvent and as an interface between the donor and acceptor phases. In this technique, called hollow-fiber membrane liquid-phase microextraction, hollow-fiber membrane may be either a u-shape with both ends connected to guiding tubes or a rod with a closed bottom. Hollow-fiber membrane liquid-phase microextraction can be performed in either the dynamic or static mode. In the static mode, the hollow-fiber membrane is immersed into the aqueous sample with the aid of a syringe, whereas in the dynamic mode the syringe with the hollow-fiber membrane is connected to a syringe pump to perform the extraction (Sarafraz-Yazdi and Amiri 2010).

Prior the extraction, the hollow-fiber membrane is immersed in an organic solvent for a few seconds to fill the wall pores with the solvent, so that it provides a supported liquid membrane. An aqueous acceptor solution is then held within its lumen. To ensure that the organic solvent remains in the wall pores of the hollow-fiber membrane during extraction without leakage to the aqueous sample, it has to be water-immiscible. Analytes are extracted first into the intermediary organic phase, represented by the membrane, and then subsequently into the aqueous phase. This system can be considered three-phase hollow-fiber membrane liquid-phase microextraction (liquid-liquid-liquid) and is preferable for extraction of ionizable compounds, which usually are then analyzed by liquid chromatography or capillary electrophoresis (Figure 3b). Several applications of three-phase hollow-fiber membrane liquid-phase microextraction employing the dynamic mode have been reported for the determination of phenoxyacetic acid herbicides (Wu et al. 2005; Chen et al. 2006).

Another mode of hollow-fiber membrane liquid-phase microextraction is based on a two-phase system in which the organic solvent fills both the hollow-fiber membrane wall pores and lumen (liquid-liquid). The two-phase mode is generally employed for hydrophobic compounds, following by gas chromatography analysis (Lee et al. 2008; Sun et al. 2011) (Figure 3a). An interesting two-phase hollow-fiber membrane liquid-phase microextraction methodology is the use of the organic solvent immobilized only in the hollow-fiber membrane pores as acceptor phase, which is desorbed after the extraction for further gas chromatography analysis. This procedure could be an alternative to the three-phase system when the fiber can be desorbed in a compatible solvent for liquid chromatography analysis, minimizing fiber handling because of the acceptor is not injected into the lumen, and only a desorption step is necessary prior chromatographic analysis (Bolaños et al. 2008). Two-phase hollow-fiber membrane liquid-phase microextraction has been applied to the analysis of pyrethroid (San Román et al. 2012), carbamate (Zhang and Lee 2006), and organochlorine (Basheer et al. 2002) pesticides in water samples. Dynamic hollow-fiber membrane liquid-phase microextraction has also been employed for the extraction of pesticides. Chen and Huang (2006) proposed a dynamic hollow-fiber membrane liquid-phase microextraction method for the extraction of organophosphorus pesticides from lake water. The extraction only required 3.5 µL of extraction solvent and 20 mL of water sample, and recoveries ranging from 83.1 to 107.0 % were achieved. The proposed procedure showed great capability and stability for the analysis of field samples and the extraction process was affected little by the sample matrix.

Figure 3

Solvents such as toluene, cyclohexane, 1-octanol and *n*-hexane are usually used as organic solvents in hollow-fiber membrane liquid-phase microextraction for pesticide extraction. Toluene is most often used as an acceptor phase in this technique due to it is immiscible with water, remains stable in the hollow-fiber membrane over the extraction time, and provides high solubility for a wide range of analytes (Lambropoulou and Albanis 2007). This solvent has been widely applied for extraction of all types pesticides, such as organophosphorus (Lambropoulou and Albanis 2005), organochlorine (Basheer et al. 2004), carbamates (Lambropoulou and Albanis 2005), and triazine herbicides (Shen and Lee 2002). Octanol has been used for extraction of more polar pesticides such as carbamates (Asensio-Ramos et al. 2012) or phenoxy herbicides (Peng et al. 2011). More recently, ionic liquids have also been proposed as extracting solvents for hollow-fiber membrane liquid-phase microextraction (Ebrahimi et al. 2011).

All hollow-fiber membrane liquid-phase microextraction methodologies have proven to be attractive as alternatives to single-drop microextraction since, besides being nearly solvent-free, simple, fast, disposable, and low cost, the hollow-fiber membrane can accommodate larger volumes of acceptor phase than droplets, which usually provides higher sensitivity and reproducibility. In addition, the small pores of the membrane function as a filter that prevents larger molecules and interfering compounds in the sample solution from being extracted into the organic solvent. Therefore, hollow-fiber membrane liquid-phase microextraction is not only a good sample enrichment technique, but also an interesting sample cleanup procedure (Sun et al. 2011; Menezes et al. 2016).

2.2.6.3 Dispersive liquid-liquid microextraction

Dispersive liquid-liquid microextraction was originally introduced by Rezaee et al. (2006) for water samples, although afterwards it has been widely demonstrated its applicability to different matrices, such as foodstuffs and soils. This technique has also been successfully applied to the specific case of extraction and concentration of a wide variety of pesticides. Dispersive liquid-liquid microextraction is based on the formation of a cloudy solution after quickly injecting and stirring a blend of extraction and disperser solvents into an aqueous sample solution (Figure 4). The large contact surface between the extractant droplets and the sample solution achieve an effective and rapid mass transfer (Ahmad et al. 2015). The extraction operation can be accomplished using a cone bottom centrifugal pipe. After centrifuging the mixture, the extraction solvent containing the analytes settles at the bottom of the pipe or collects on the top of the extraction vessel based on its density. Dispersive liquid-liquid microextraction is usually coupled with gas chromatography or liquid chromatography.

Figure 4

In dispersive liquid-liquid microextraction, the extraction and disperser solvents used usually are nonpolar water-immiscible and polar water-miscible, respectively. Water immiscible and high density extracting solvents have been the commonly used extraction solvents for pesticides, such as chlorobenzene (Berijani et al. 2006; Zhao et al. 2007), chloroform (Liu et al. 2009), and carbon tetrachloride (Zhao et al. 2008). Because these solvents are highly toxic and are limited in extracting various analytes with different polarities, with the development of dispersive liquid-liquid microextraction polar and low-density organic solvents and some environmentally friendly ionic liquids have also been used as extractants, such as *n*-hexane (Moinfar and Hosseini 2009), cyclohexane (Farajzadeh et al. 2009), undecanol (Sanagi et al. 2012), 1-octyl-3-methylimidazolium hexafluorophosphate (Liang et al. 2013), and 1-benzyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (Wang et al. 2016). Several homemade special extraction devices were used for collecting organic solvents with a density lower than water after extraction. The task of dispersant in dispersive liquid-liquid microextraction is to disperse the extraction solvent into small organic droplets, so that the volume of the extractant droplet decreases, and the surface area of the extractant increases. Acetone (Berijani et al. 2006) and acetonitrile (Zhao et al. 2007) have been the main options as disperser solvents.

A new mode of dispersive liquid-liquid microextraction based on solidification of floating organic droplet appeared to solve the extraction device problem for low-density organic solvents (Wang et al. 2019). The extractant used in this mode is a low density and low melting point organic solvent (10–30 °C), and no specific holder is necessary to collect it. After the extraction process, the extraction device is placed in an ice bath to solidify the extractant phase, and this latter is collected and melted for further analysis (Leong and Huang 2009; Wu et al. 2010). However, an additional cooling step is required in this methodology.

The main drawback of dispersive liquid-liquid microextraction is the consumption of large volumes (i.e. mL) of disperser solvent and that its presence increases solubility of analytes in the aqueous phase, which results in relatively low extraction efficiency. Several progresses have been made to overcome this, such as the introduction of ultrasound-assisted dispersive liquid-liquid microextraction. In this variant of dispersive liquid-liquid microextraction, under the action of ultrasonic waves, an emulsion system of extractant/water is formed only by ultrasonic treatment without dispersant (Regueiro et al. 2008; Liang et al. 2013). A new dispersive liquid-liquid microextraction mode called vortex-assisted liquid–liquid microextraction was introduced by Yiantzi et al. (2010), which made use of vortex mixing for the dispersion of low density extraction solvents in water. The floating extractant phase could restore its first single-drop shape after extraction and be collected. However, among the solvents tested, only 1-octanol was able to restore its single-drop shape. This approach was later successfully applied for the extraction of pesticides in water samples by using hexane as an extraction solvent. Acceptable recoveries over the range of 72–106.3% were obtained (Jia et al. 2010). Another interesting modification of dispersive liquid-liquid microextraction was developed, which consisted in performing the dispersion of the extraction solvent in the sample solution during suction/injection cycles with a glass syringe. This disperser solvent-free methodology was called air-assisted liquid-liquid microextraction (Farajzadeh and Mogaddam 2012). Air-assisted liquid-liquid microextraction was applied for the assessment of triazole pesticides residues in surface water, cucumber, tomato and grape juices samples (Farajzadeh and Khoshmaram 2013). The proposed methodology eliminates both drawbacks of dispersive liquid-liquid microextraction by using a low-density extraction solvent along with the formation of a cloudy state in the absence of a disperser solvent. Other recent applications of air-assisted liquid-liquid microextraction are the extraction of organophosphorus pesticide residues in fruit juice samples (You et al. 2013), fungicides from environmental water and juice samples (Wu et al. 2015), triazole and triazine pesticides from honey (Farajzadeh et al. 2014) or triazole pesticide residues in edible oils (Farajzadeh et al. 2015).

The large number of publications is evidence that dispersive liquid-liquid microextraction is principally applied to pesticide residue analysis (Ahmad et al. 2015) and that they are mostly analyzed in aqueous samples. Gas chromatography is the most appropriate technique for further separation and determination of pesticides after dispersive liquid-liquid microextraction, although liquid chromatography has also become a popular technique for this purpose. However, in liquid chromatography a reconstitution of the extract in a solvent more compatible with liquid chromatography columns is usually required. Other techniques like micellar electrokinetic chromatography have also been successfully used in combination with dispersive liquid-liquid microextraction (Zhang et al. 2010; Zhang et al. 2011).

Dispersive liquid-liquid microextraction has also been successfully applied for extraction of pesticides in solid samples. Examples of these applications are the analysis of carbamate pesticides in apple (Zhang et al. 2010), organophosphorus pesticides in fruits and vegetables (Ho et al. 2013), sulfonylurea herbicides in soil (Zhang et al. 2011), neonicotinoid insecticides in cucumber (Zhang et al. 2012a), carbamate pesticides in watermelon and tomato (Liu et al. 2012) or pyrethroids in soil (Wang et al. 2012b). In most cases when samples are solid such as vegetables and fruits, their juices are extracted and the extraction procedure is performed on these juices. However, a portion of analytes may remain in the refuse of samples and be discarded. Very recently, to overcome this difficulty some authors proposed to combine QuEChERs and dispersive liquid-liquid microextraction for the extraction and preconcentration of analytes (Farajzadeh et al. 2019), so that the adsorbed analytes onto the refuse of the samples are desorbed by the same solvent that is used as dispersant (acetonitrile) in the following preconcentration procedure. Thus, the combination of dispersive liquid-liquid microextraction with QuEChERs for sample preparation widens its application to those samples with complex matrices.

Dispersive liquid-liquid microextraction is a very versatile technique, since it can be applied to nearly all classes of compounds and combined directly or after solvent replacement with most pre-concentration methodologies. On the other hand, dispersive liquid-liquid microextraction for analysis of pesticides shows several advantages, such as high recoveries and high enrichment factors, low consumption of organic solvents, low cost, ease to perform, and short time of analysis.

2.3 Solid-phase extraction techniques

2.3.1 Solid-phase extraction

Solid-phase extraction was introduced in the mid-1970s and came to prominence in the 1980s. In the last years, solid-phase extraction has been one of the most commonly used sorbent techniques for pesticide residue analysis. It has been proven that solid-phase extraction shows several important advantages over traditional liquid-liquid extraction, such as reduction of solvent consumption, shorter time of analysis, no phase emulsions, better enhancement factors, and more effective removal of interfering species. Both solid-phase extraction and liquid-liquid extraction are frequently combined to achieve better enrichment and cleanup. Extraction is performed by passing the sample through a particulate or monolithic sorbent packed into columns of short length, usually called ‘cartridges’, or immobilized in the form of a thin disc. Solid-phase extraction can be used either manually or with greater throughput using automated workstations.

There is a wide choice of sorbents for solid-phase extraction, including polar, nonpolar and mixed mode sorbents that provide the selectivity necessary to obtain clean extracts for pesticide analysis. The conventional sorbents used in solid-phase extraction are chemically modified silica gel (C_2, C_8, C_{18}) graphitized or porous carbon, and polymer sorbents (Rastrelli et al. 2002; Poole 2003; Zheng et al. 2014), which show low retention for polar compounds. More recently, hydrophilic polymeric sorbents, such as Oasis HLB or Porapak RDX, have been used which, as a general rule, have a high specific surface area and improve the extraction efficiency of polar compounds (Fontanals et al. 2005; Bratkowska et al. 2010).

Most developments in solid-phase extraction technique have been directly related to the improvement of sorbent materials. Efforts have been made to make magnetic the sorbent material, which permits an easy removal of the extraction medium from the sample solution by using a magnet (Wan Ibrahim et al. 2015; Bagheri et al. 2016). Further developments incorporated nanoparticles that were shown effective due to the high surface area to volume ratio, which allows rapid adsorption of analytes (Yu and Yang 2017). Rashidi Nodeh et al. (2017) synthesized a graphene-based tetraethoxysilane-methyltrimethoxysilane sol-gel hybrid magnetic (Fe_3O_4@G-TEOS-MTMOS) nanocomposite that was applied as adsorbent in solid-phase extraction for simultaneous determination of polar and nonpolar organophosphorus pesticides from different water samples. Good recoveries between 83 and 105 % were obtained. New materials as carbon nanotubes, both multi-walled and single-walled carbon nanotubes, have also been successfully applied for cleanup purposes (López-Feria et al. 2009). These materials have an extremely large surface area and unique structure, so that they have excellent adsorption ability. Carbon nanotubes have been proposed as a kind of sorbents in a packed column, and applied for extraction of pesticides from water samples (Zhou et al. 2006; Wang et al. 2007a; El-Sheikh et al. 2008). Du et al. (2008) developed a new analytical method to determinate organophosphate pesticides in garlic by extraction with multi-walled carbon nanotubes. Ravelo-Pérez et al. (2008b) also demonstrated that multi-walled carbon nanotubes can be used as effective solid-phase extraction materials for the extraction of pesticides from apple, grape, orange and pineapple fruit juices.

On the other hand, molecularly imprinted polymers have also been used for selective solid-phase extraction, since they yield specific binding sites within a polymeric matrix and are also helpful in cleaning up complex matrices. The first attempt on the development of a dual methodology for the trace analysis of pesticide residues based on molecularly imprinted polymer technology was recently reported. The method was developed for the simultaneous analysis of dimethoate and terbuthylazine residues in olive oil samples, and was based on the use of a dual layer of 'tailor-made' molecularly imprinted polymers as solid-phase extraction sorbent. High recovery rates for dimethoate (95%) and terbuthylazine (94%) were achieved with good accuracy and precision (Garcia et al. 2016).

The introduction of new sorbents with more selective modes of attraction, novel product formats such as the solid-phase extraction disc, and the proliferation of automated techniques for performing the extractions, ensure that solid-phase extraction will continue to be a preferred technique for sample preparation in many different analytical disciplines.

2.3.2 Dispersive solid-phase extraction: QuEChERS

Solid-phase extraction technique includes several steps, is time-consuming and requires much organic solvent volume than other modern techniques recently reported. Moreover, sometimes several packed columns with different sorbents are required to obtain good results. To overcome these drawbacks, Anastassiades et al. (2003) developed a simple and rapid cleanup technique for fruits and vegetables named dispersive solid-phase extraction. In this new approach, the sample extract was not passed through a solid-phase extraction column but the matrix interfering species were removed by adding an amount of sorbent material to the extract. Then, the sorbent was separated from the extract by centrifugation. The main advantages of this new methodology compared with solid-phase extraction were: the possibility of using a much smaller quantity of sorbent and solvent, a shorter time of analysis, and a simpler procedure (Fontana et al. 2011). In the original method proposed by Anastassiades et al. dispersive solid-phase extraction was combined with a previous extraction, giving rise to the QuEChERS method, which is defined as a simple, fast, safe, rugged, effective and inexpensive method for the multiclass or multiresidue analysis of pesticides. Over the years, dispersive solid-phase extraction has been used as an independent cleanup methodology (Nguyen et al. 2010; Dias et al. 2016), although in most of the cases, has been applied as a part of QuEChERS method.

QuEChERS combines the extraction/isolation and extract cleanup of both nonpolar and polar pesticides simultaneously from food matrices. The optimized procedure consisted of several steps: 1) an initial extraction step in which the minced and homogenized sample (10 g) was extracted with acetonitrile (10 mL); 2) an extraction/partitioning step by means of the addition of salt mixture (4 g of anhydrous $MgSO_4$ and 1 g of NaCl) and; 3) a dispersive solid-phase extraction cleanup step of an aliquot of the extract (1 mL) with 25 mg of N-propylethylenediamine (primary secondary amine) and 125 mg of $MgSO_4$. Finally, the extract was directly transferred to a vial for gas chromatography-mass spectrometry analysis. In these working conditions, recovery values between 85 and 101 % for more than 95 % of pesticides were achieved. Although the usual solvents for analysis of pesticides in food matrices have been ethyl acetate (Fernandez-Alba et al. 1994; Mol et al. 2007; Banerjee et al. 2007), acetone (Guan et al. 2010) and acetonitrile (Fillion et al. 2000; Lehotay et al. 2001), this latter was selected in the QuEChERS methodology as the most appropriate solvent due to its clear advantages over the others. Although acetonitrile is miscible with water, a phase separation is possible by addition of salts. Besides, the remaining water can be easily eliminated by adding a drying agent like $MgSO_4$. However, acetone cannot be separated from water without using nonpolar solvents. As for ethyl acetate, it can be easily separated from water since both solvents are partially miscible, but it is not a good solvent for most very polar pesticides. Additionally, many lipophilic compounds such as fats, pigments and waxes are not extracted in acetonitrile compared to acetone and ethyl acetate (Wilkowska and Biziuk

2011). Different salts were evaluated to induce a phase separation in the extraction/partitioning step. The most effective salt with respect the recovery of analytes resulted to be $MgSO_4$. Moreover, the addition of this salt facilitated the partition of very polar pesticides like acephate, methamidophos or omethoate into the organic phase, since the volume of the aqueous phase was effectively reduced. Selectivity of the extraction procedure, that is, the polarity range of the method, can be controlled through the amount of NaCl added in the partitioning step with $MgSO_4$. The cleanup of the extract using dispersive solid-phase extraction with primary secondary amine allowed efficiently removing many polar interfering species coming from the matrix like organic acids, fatty acids, some sugars and polar pigments.

Liquid chromatography was not used in the initial QuEChERS method, thus the applicability of this approach to very polar and thermally labile pesticides was not evaluated. Later, Lehotay et al. (2005a) continued the researches of Anastassiades et al. and introduced some modifications to validate the application of the QuEChERS methodology to the analysis of 229 pesticides in lettuce and orange matrices using concurrent large volume injection (LVI)/gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry in tandem detection. In the original method the first extraction step was carried out in unbuffered solutions. Under such conditions, the use of primary secondary amine in the cleanup step can originate losses of pH-sensitive pesticides (base-labile compounds) due to their hydrolization under basic conditions. To overcome this drawback, Lehotay et al. (2005a) added 0.1 % glacial acetic or formic acid solutions after the extraction process. Later, different modifications of the QuEChERS method were proposed for improving stability of pH-dependent pesticides in the final extracts. As a consequence of these efforts, two official methods for pesticide residue analysis were developed, AOAC Official Method 2007.01 (AOAC 2007) and CEN Standard Method EN 15662 (European Committee for Standardization 2008), in which acetate and citrate buffers (pH= 5) are included in the extraction step, respectively. Both methods allowed obtaining recoveries higher than 70% for acid-sensitive pesticides without affecting the base-sensitive pesticides.

Since its introduction, the QuEChERS method has undergone many other modifications with the purpose to improve sensitivity and recovery of specific types of pesticides, and reduce the matrix effect. There are two factors mutually related to each other that play a relevant impact on the recovery of the target compounds in QuEChERS, as follows: (a) the solvent used for extraction and (b) the type and amount of salts and sorbents for dispersive solid-phase extraction. Other solvents as substitutes for acetonitrile have been tested for the extraction step, such as hexane/acetone or acetonitrile/hexane (Cheng et al. 2016). Regarding the salts for partitioning and salting-out effects, $MgSO_4$ (0.5-10 g) and NaCl (0.2-6 g) are the most frequently used (Santana-Mayor et al. 2019) although other salts such as $CaCl_2$ and Na_2SO_4 have also been tested. For dispersive solid-phase extraction step, the sorbent is chosen to retain the matrix components and allow the analytes of interest to remain in the liquid phase.

Although the QuEChERS method was initially developed for samples with high content in water (80-95 %) such as vegetables and fruits, afterward it has been applied to other matrices. In the case of samples with water content <80 % it is necessary the addition of water at the beginning of the process. A method was developed for the analysis of pesticide residues in foods containing up to 20% fat (milk, avocado and eggs). In this kind of foods, both hydrophilic and lipophilic pesticides could be found and, therefore, the development of a methodology able to simultaneously determine analytes with a wide range of polarity was essential (Lehotay et al. 2005b). The authors demonstrated that the combined use of primary secondary amine with octadecylsilane in these matrices was especially effective, since this latter removes non-polar interfering species like lipids. An additional freeze-out step to reduce interfering lipids and, in addition, other matrix component co-extractives with poor solubility was also proposed. Nevertheless octadecylsilane demonstrated to be faster, easier, and equally effective in removing lipids (Walorczyk 2008). Another interesting alternative is the use of chitin, a new cleanup sorbent introduced by Cerqueira et al. (2014), which exhibits various bioactivities and functionalities. The authors proposed it for the dispersive solid-phase extraction step of the QuEChERS process for the simultaneous extraction of simazine, atrazine, clomazone and tebuconazole, and other organic contaminants in drinking water treatment sludge samples by employing liquid chromatography-tandem mass spectrometry. This sorbent has shown to be more efficient than the combination primary secondary amine/octadecylsilane for multiclass pesticide residue analysis in matrices such as fish liver and muscle, since it reduced background effectively without significantly reducing recovery of lipophilic pesticides such as organochlorine and some pyrethroids (Kaczyński et al. 2017). Moreover, it is cheaper because it is obtained from natural sources.

Another important aspect to take into account was the co-extraction of pigments in some samples, such as spinach and other highly pigmented vegetables. The addition of a small amount of graphitized carbon black (as in the CEN Standard Method EN 15662 (European Committee for Standardization 2008) combined with primary secondary amine improved the results, although the strong affinity of graphitized carbon black for planar molecules (chlorophyll, carotenoids or sterols) also reduced in approximately a 25 % the recovery of structurally planar pesticides (i.e. thiabendazol, terbufos, hexachlorobenzene, etc.). An alternative to graphitized carbon black, a cross-linked polymeric sorbent called ChloroFiltr®, was designed that effectively eliminated chlorophyll without affecting the planar pesticides (Łozowicka et al. 2017; Rutkowska et al. 2018). Multi-walled carbon nanotubes have also been proposed as effective sorbents in the dispersive solid-phase extraction step of the QuEChERS method to remove pigments from vegetables (Zhao et al. 2012) owing to its unique structure and the huge surface area (Iijima 1991; Ren et al. 1998). The method was validated for determination of 30 representative pesticides in cabbage, spinach, grape and orange spiked at concentration levels of 0.02 and 0.2 mg kg^{-1}. The recoveries were between 71 and 110%, with relative standard deviations < 15%.

The QuEChERS method has also been applied to the pesticide residue analysis in high fat content foods such as almond, avocado, edible vegetable oils or olives (Cunha et al. 2007; Lozano et al. 2014; He et al. 2017; Manav et al. 2019). In these matrices, analytes are mainly nonpolar, so there is no need to develop analytical methods for determining polar pesticides. The main components of vegetable oils are lipids, pigments and fatty acids. Therefore, the sample treatment in these highly complex matrices for pesticide residue analysis is still a challenge, since the high molecular-mass fat from the sample has to be completely removed in order to avoid damages to the chromatographic system. A modified QuEChERS method using amine modified graphene (CH_3NH-G) material for the dispersive solid-phase extraction step was proposed by Guan et al. (2013) and applied to the determination of pesticide residues in four oil crops obtaining recovery percentages between 70.5 and 100 % and low limits of detection (0.1-8.3 μg kg^{-1}). These amine modified graphene materials have a high surface area and amine groups forming strong hydrogen bonds with carboxylic acid groups. Therefore, they are effective cleanup sorbent in pesticide multiresidue analysis in high-fat (>20%) commodities and show better performance than primary secondary amine, graphitized carbon black and multi-walled carbon nanotubes (Hakme et al. 2018).

Recently, new sorbents based on zirconium oxide such as zirconium oxide-based sorbent (Z-Sep), zirconium oxide-based sorbent/octadecylsilane (Z-Sep^+) and yttria-stabilized zirconium dioxide nanoparticles (ZrO_2/Y_2O_3) have demonstrated to have a higher capacity than primary secondary amine, octadecylsilane and graphitized carbon black sorbents to remove fatty acids, esters of fatty acids, carboxylic acids, sterols and pigments from high oil matrices (Lozano et al. 2014). The new lipid-removal sorbent zirconium oxide-based sorbent/octadecylsilane (Z-Sep^+) was evaluated for the analysis of carbamate pesticides in edible vegetable oils and high-fat cheeses by tandem mass spectrometry combined with ultra-high performance liquid chromatography, providing a significant removal of co-extractive interferences and excellent recoveries (Moreno-González et al. 2014; Hamed et al. 2017). In this commercially available product zirconium binds to the polar groups of the lipids through Lewis acid-base interactions and octadecylsilane binds hydrophobic chains of the lipids (Hakme et al. 2018). It is necessary to take into account that with this type of sorbents nonpolar pesticides could also be removed in the cleanup step (Moreno-González et al. 2014; Tuzimski and Rejczak 2016).

One of the most novel sorbents for dispersive solid-phase extraction, EMR-Lipid, was introduced by a vendor for removing interfering lipids from samples while leaving analytes behind. The structure of EMR-Lipid is a proprietary secret, and its action mechanism in dispersive solid-phase extraction process involves a combination of hydrophobic interactions and size exclusion between the long chain of lipids and the sorbent. It dissolves to saturation in the extracts and then, the lipid-EMR-Lipid complex is precipitated out or remains in the aqueous phase during the salting-out step (Han et al. 2016). Parrilla-Vázquez et al. (2016) and Dias et al. (2016) used EMR-Lipid as a highly selective sorbent to remove lipids in the multiresidue analysis of pesticides in edible vegetable oils. The proposed procedures showed good recoveries (70-120%), low limits of quantitation (10-50 μg kg^{-1}) and low relative standard deviations (< 20 %). The EMR-Lipid showed as the only disadvantage the use of a higher amount of the extract when compared to the other approaches (primary secondary amine and zirconium oxide-based sorbent (Z-Sep)). Han et al. (2016) also evaluated the novel commercial EMR-Lipid product for cleanup of kale, salmon, avocado, and pork extracts for multiclass, multiresidue analysis of 65 pesticides and other environmental contaminants. The sorbent efficiently removed 79-98 % of co-extracted matrix compounds, providing clean extracts and low background in gas chromatography-tandem mass spectrometry analysis. Moreover, up to a 76% of the co-extracted chlorophyll was removed without loss of co-planar pesticides. The use of ‘Analyte Protectants’ after dispersive solid-phase extraction with EMR-Lipid sorbent has been evaluated in order to minimize the matrix effect during injection into the gas chromatography system. Analyses of pesticides by gas chromatography are frequently affected by degradation problems and peak tailing associated with the active sites on the surface of the stationary phases. ‘Analyte Protectants’ are mixtures of compounds containing multiple hydroxyl groups, whose function is to mask these active sites by making hydrogen bonds through their hydroxyl groups and thus protecting the analytes (Sanchez Costa et al. 2018). Other novel dispersive solid-phase sorbents have been very recently developed by different companies, such as Cleanert® NANO or LipiFiltr®, whose efficiency in the improvement of the dispersive solid-phase step in the QuEChERS procedure will have to be assessed in the next years.

Nowadays, the expansion of the QuEChERS method and its establishment practically as a universal method for routine analysis of pesticide residues in food products has led to the commercialization by several companies of the different products involved in the procedure (salts, buffers, sorbents) in the form of kits, so that the time of analysis is significantly reduced.

2.3.3 Matrix solid-phase extraction

Matrix solid-phase dispersion was developed by Barker et al. (1989) to carry out extraction of target analytes from solid matrices, and overcome the serious restrictions on solid-phase extraction methods for this kind of samples. The key characteristics for the success of matrix solid-phase dispersion are its feasibility, flexibility, versatility, low cost and rapidity and, over the past years, it has been widely used for extraction of pesticides from both vegetable and animal matrices (Wang et al. 2015). In this technique, the solid or semi-solid sample is mixed with an appropriate adsorbent with the aid of a mortar and pestle, which causes the disruption and dispersion of the analytes on the solid support. Then, the blend sample-adsorbent is added to a column/cartridge and the analytes are eluted with an appropriate solvent. An additional cleanup of the sample can be carried out by packing in the bottom of the same column/cartridge another adsorbent. Thus, this technique allows performing, on a small sample aliquot, extraction and cleanup in a single step. Even if matrix solid-phase dispersion has many characteristics in common with classical solid-phase extraction, the mechanism governing the two processes is quite different. The main difference between both techniques is the physical state of samples applied to the column, since whereas in solid-phase extraction samples are liquid (solution) in matrix solid-phase dispersion samples are solid. Generally, after matrix solid-phase dispersion, a liquid chromatography or gas chromatography separation is followed by mass spectrometry determination. Although matrix solid-phase dispersion was initially introduced for disrupting and extracting solid samples, it has also been applied to semi-solid and viscous samples. Otherwise from other classical extraction methodologies, matrix solid-phase dispersion does not require a large amount of sample, sorbents and organic solvents, is not laborious, is rapid, and more environmentally-friendly. An additional cleanup step can be required or not after the extraction depending on the analytes and the instrumental analytical technique used for the analysis.

Carbon based sorbent materials such as octylsilane and octadecylsilane are the most frequently used sorbents, since they provide a good disruption and dispersion of the sample because their lipophilic characteristics (Rodrigues et al. 2010). Other adsorbents such as Florisil (Łozowicka et al. 2012), graphitized carbon black (Barriada-Pereira et al. 2010) and silica have also been frequently used. Aminopropyl, followed by cleanup with Florisil, has also been successfully applied as sorbent material for multiresidue pesticide analysis in olives by gas chromatography–mass spectrometry and liquid chromatography–tandem mass spectrometry determination. The most recent innovation introduced in matrix solid-phase dispersion over the past few years has been the use of novel supporting materials, such as multi-walled carbon nanotubes and nanomaterials (Capriotti et al. 2013). Fang et al. (2009) decided to evaluate the efficiency of multi-walled carbon nanotubes in matrix solid-phase dispersion applications, and they use them as dispersant to extract 31 pesticides from agriculture samples before gas chromatography-mass spectrometry determination. The authors found that the extracts obtained by using multi-walled carbon nanotubes were cleaner than those obtained by using diatomite and octadecylsilane as dispersant materials, with recoveries above 71% for both apple and potato samples. Another interesting alternative to the classical matrix solid-phase dispersion is the use of hydrophobic magnetic octadecylsilane-based nanoparticles, which was applied for the multiresidue determination of 26 pesticides in carrots (Binellas and Stalikas 2015). The magnetic nanoparticles could be removed from the solution by *n*-octanol and application of a magnetic field. The extracts were then directly analyzed by gas chromatography-mass spectrometry without needing a previous cleanup step. The average extraction recoveries were 77-107 % and the limits of quantitation for most pesticides were in the low μg kg^{-1} level. Very recently, other authors proposed, for the first time, the integration of magnetic ionic liquids into a matrix solid-phase dispersion procedure for the analysis of multi-class pesticide residues in potatoes and other vegetables (Chatzimitakos et al. 2018). The viscous nature of the selected magnetic ionic liquids assists in blending with the matrix, while their hydrophobic properties facilitate easier separation and retrieval. Moreover, they can be removed magnetically. The raw vegetables were analyzed without any other pretreatment prior to or after extraction, without the need for solid dispersing materials or co-sorbent for cleanup.

Of all the features of matrix solid-phase dispersion above described, it can be considered as a valid alternative to Soxhlet and microwave-assisted extraction, as well as pressurized liquid extraction and supercritical fluid extraction. In fact, compared to these techniques, matrix solid-phase dispersion requires mild extraction conditions (room temperature and atmospheric pressure) as well as it provides suitable yield and selectivity. Moreover, matrix solid-phase dispersion is a good alternative to solid-phase extraction for the analysis of solid samples. Development of new sorbent materials for improving the capacity or selectivity is still the exciting research area in this technique.

2.3.4 Solid-phase microextraction

Solid-phase microextraction is a sorption-based microextraction methodology in which a concentration equilibrium between the target analyte(s) in a sample and a sorptive phase occurs. It was introduced in 1990 (Arthur and Pawliszyn 1990), and since then it has undergone a rapid development. In most traditional approaches to solid-phase microextraction, the extraction of organic compounds can be performed in two different modes, by immersing an externally polymer-coated fiber in sample solution, the so-called direct immersion solid-phase microextraction, or exposing this fiber to the headspace above the samples, the so-called headspace solid-phase microextraction (Ai 1997). The solid-phase microextraction device is constructed of a thin fiber (< 50 μm), which is used as substrate/support for a thin layer (5–100 μm) of a suitable sorptive (extraction) phase. Solid-phase microextraction uses a fiber coated with a liquid (polymer), a solid (sorbent), or a combination of both. Analytes are extracted from sample by absorption or adsorption, depending on the nature of the fiber coating. Coating thickness determines the volume and surface area of sorptive phase and consequently, the amount and rate of absorption. For further chromatographic analysis, the fiber can be directly put into the injection port of a gas chromatography instrument (thermal desorption) or immersed into an appropriate solvent (chemical desorption) for gas chromatography or liquid chromatography analysis. In-tube solid-phase microextraction is an automated version of solid-phase microextraction that allows its easy coupling with liquid chromatography, and it has proven to be a very efficient extraction method for the analysis of polar and thermally labile pesticides (Eisert and Pawliszyn 1997). This mode of solid-phase microextraction typically uses a gas chromatography capillary column with an appropriate extraction phase coated on its internal surface to extract the analytes (Gou et al. 2000).

Popularity of solid-phase microextraction within the analytical community has been continuously increasing since its first introduction, generating applications encompassing a multitude of compounds and matrices in a large variety of fields (Lashgari and Yamini 2019). This technique integrates sampling, extraction, concentration and sample introduction into a single step. Moreover, solid-phase microextraction requires minimal or zero amounts of solvent, which distinguishes it a 'greener', more environmentally-friendly technique in comparison to other sample preparation techniques. Therefore, solid-phase microextraction gathers most of the required features for pesticide analysis in food and environmental matrices, that is, to cover a wide scope of pesticide–matrix combinations, provide a certain grade of selectivity, be rapid, and be easy to carry out (Souza-Silva et al. 2015b; Souza-Silva et al. 2015a). In fact, it has become a routine technique in many laboratories due to it can be fully automated, is easy to miniaturize, and is convenient in coupling with chromatographic instruments.

One of the key steps in the development of a solid-phase microextraction method for analysis of pesticides is the selection of an appropriate fiber coating based on their nature and volatility. Thin fibers are used for pesticides with high boiling points and thicker fibers are suitable for volatile pesticides. Polydimethylsiloxane (Neuwirthová et al. 2019) and poly(acrylate) (Fernandez-Alvarez et al. 2008) coated fibers have been used for years as general-purpose sorbents for pesticide residue analysis. Nowadays, a great variety of more specific fiber coatings based on solid sorbents is available in the market, that include: Carbowax/template resin (Blasco et al. 2011), polydimethylsiloxane/divinylbenzene (Ravelo-Pérez et al. 2008a; Zhang et al. 2018), and polydimethylsiloxane/poly(acrylate) (Fernandez-Alvarez et al. 2009) coated fibers. For over a decade since the introduction of direct immersion solid-phase microextraction, it only could be applied to extraction of analytes from very simple matrices or complex matrices subjected to multiple cleanup steps, since the available coating surfaces suffered an irreversible attachment of macromolecules from the matrix samples, which decreased the extraction efficiency. Solid coatings frequently suffer from an irreversible fouling effect or sorption of unwanted matrix components, which is less frequent in liquid coatings. Thus, for years the liquid polydimethylsiloxane coating was the most used sorbent for the direct immersion solid-phase microextraction of pesticide residues in food matrices (Beltran et al. 2000). Therefore, many solid-phase microextraction applications to food and environmental samples had to be carried out by headspace solid-phase microextraction mode since matrix compatible coatings were not available.

Liquid coatings are better than solid coatings in regards to the fouling effect, but these latter show higher extraction efficiency because the rough morphology of their surfaces. Moreover, liquid coatings are not good sorbents for semi-polar and polar compounds. To overcome these limitations and take advantage of the properties of both types of coatings, in the last years a great variety of porous sorbents have been prepared by combining liquid and solid coatings, which can withstand direct exposure to complex matrices and are described as 'matrix compatible' (Godage and Gionfriddo 2019). Souza Silva and Pawliszyn (2012) developed a new type of solid-phase microextraction fiber coating, polydimethylsiloxane/divinylbenzene/polydimethylsiloxane, which was obtained modifying commercial solid-phase microextraction fiber coatings by incorporation of an additional protective thin layer of polydimethylsiloxane. This coating was more robust, prevented wicking of matrix components and analytes into the fiber core, and allowed up to 100 extractions of triazole pesticides in water samples and grape pulp by direct immersion solid-phase microextraction with no sample treatment. The polydimethylsiloxane/divinylbenzene /polydimethylsiloxane coating also showed excellent robustness and matrix compatibility with oily matrices for the extraction of multiclass pesticides and other contaminants by direct immersion solid-phase microextraction in avocado pulp (De Grazia et al. 2017). Its extraction efficiency remained constant for more than 100 extraction runs, whereas the extraction efficiency of divinylbenzene/polydimethylsiloxane coating showed a severe decrease after only 20 successive extractions. Polydimethylsiloxane/divinylbenzene/polydimethylsiloxane coating has also been employed in the direct coupling of solid-phase microextraction to mass spectrometry for pesticide residue analysis in food and environmental samples (Mirabelli et al. 2018). This coating showed matrix compatibility and excellent antifouling properties, taking into account that this coupling solid-phase microextraction-mass spectrometry does not involve chromatography and, therefore, it is mandatory that the coatings prevent sorption of matrix components which could drastically affect the ionization process.

The use of solid-phase microextraction fibers presents some other limitations: coatings have usually poor thermal stability, so that the gas chromatography injector temperature has to be maintained below the maximum operating temperature of the coating (usually 240–280°C); in organic solvents coatings are unstable and suffer swelling, which restricts their use with liquid chromatography; and fibers have to be conditioned before using, are fragile and have a short lifetime due to the irreversible sorption of high molecular weight compounds. In the past decade, there has been a growing interest in the use of polymeric ionic liquids, a novel class of solid-phase microextraction coatings (Yu et al. 2013). These sorbents present interesting features as high viscosity, thermal stability, and compatibility with gas chromatography. Moreover, ionic liquids are often referred as ‘designer solvents’, since millions of them can be formed through different combinations of anions, cations, and other functional groups. This unique property allows developing ionic liquids with an enhanced selectivity towards the target pesticides. In recent years, several applications of direct immersion solid-phase microextraction to analysis of pesticides in food and environmental matrices have been reported. Recently, Zhang et al. (2012b) reported a new ionic liquid, namely, 1-vinyl-3-hexadecylimidazolium hexafluorophosphate, for the determination of seven pyrethroids in vegetables by direct immersion into hexane extracts, followed by gas chromatography-electron capture detection. Multi-walled carbon nanotubes have also found application as solid-phase microextraction coating fibers. In a recent study, pyrethroid pesticide residues in tea brew were extracted without prior sample treatment with multi-walled carbon nanotubes solid-phase microextraction fibers, which were formed by a stainless steel core coated with polyacrylonitrile solution as a binder, providing recoveries between 94.2% and 107.3% for spiked samples (Ren et al. 2018). Nevertheless, the matrix compatibility of this new solid-phase microextraction coating still needs to be assessed.

The application of solid-phase microextraction for pretreatment samples with a complex composition, as a previous step before the chromatographic analysis of pesticides and other organic contaminants, is continuously increasing. Moreover, solid-phase microextraction is an environmentally-friendly sample preparation technique that meets the sustainability requirements, and concretely those derived from the application of green analytical chemistry. Owing to all these features, to its flexibility and possibility of being combined with a great variety of analytical techniques, it is expected that the evolution of this technique in the coming years will not have limits.

2.3.5 Stir bar sorptive extraction

Stir bar sorptive extraction was introduced by Baltussen et al. (1999) to deliver more sorptive-phase mass and surface area. The extraction mechanism is similar to that of solid-phase microextraction, that is, a sorptive interaction of usually a coating of polydimethylsiloxane deposited on a magnetic glass with the target compounds (Figure 5). Stir bar sorptive extraction was developed by Gerstel GmbH & Co. KG (Mülheim an der Ruhr, Germany) and commercialized under the trade name Twister®. The stir bar is immersed in the liquid sample to be analyzed, which is shaken for a given time. While stirring, the bar adsorbs the target compounds, and then it is removed from the sample, rinsed with deionized water and dried. Then, the retained compounds can be desorbed with a suitable solvent for gas chromatography or liquid chromatography analysis. On-line thermal desorption can be also used for thermally stable semi-volatile and volatile compounds and gas chromatography analysis.

Figure 5

Stir bar sorptive extraction overcomes the main drawback of solid-phase microextraction, which is the low amount of available polydimethylsiloxane phase (~0.5 µL; 100 µm film thickness). In stir bar sorptive extraction the amount of phase typically coated is 24–126 µL and, consequently, much higher recoveries can be reached and sensitivity is increased by a factor of 50 and 250, reducing detection limits to sub-ng L^{-1} levels (Chaves et al. 2007). Moreover, stir bar sorptive extraction shows good blank levels and no degradation after 100 extractions (Zuin et al. 2006). In recent years, stir bar sorptive extraction has become one of the most studied sample extraction techniques for analysis of organic compounds. Originally, this extraction technique was intended to screen priority organic micro-pollutants in water samples (León et al. 2003; Sandra et al. 2003), but over time, applications for almost every field of analytical chemistry have been developed (Campillo et al. 2010; Li et al. 2012). Organophosphorus pesticides in vegetables were determined by stir bar sorptive extraction and gas chromatography with thermionic specific detection by using as extraction phase a hydroxy-terminated polydimethylsiloxane prepared by sol–gel methodology. The linear ranges were 0.05–50 ng g^{-1} with detection limits ≤0.15 ng g^{-1} (Liu et al. 2005). Sandra et al. (2001) used stir bar sorptive extraction followed by thermal desoption or liquid desorption for the analysis of dicarboximide fungicides in wines. A multiresidue method based on stir bar sorptive extraction followed by gas chromatography-mass spectrometry, by applying a new thermal desorption unit, fully automated, allowed the determination of more than 300 pesticides in baby food, vegetables and fruits (Sandra et al. 2003). Micellar electrokinetic chromatography–diode array analysis has also been applied in combination with stir bar sorptive extraction for the simultaneous extraction of pesticides (acrinathrin, bitertanol, cyproconazole, fludioxonil, flutriafol, myclobutanil, pyriproxyfen, and tebuconazole) in vegetables samples (Juan-García et al. 2005).

Stir bar sorptive extraction presents some drawbacks such as the limited range of analyte polarities for the available stationary phases, the presence of strong matrix effects, the requirement of a strict control of extraction parameters (Camino-Sánchez et al. 2014) and the complexity in the automation of the desorption step, especially to liquid chromatography (Chaves et al. 2007). At present, polydimethylsiloxane and ethylene glycol-silicone are the only commercially available phases in stir bar sorptive extraction. A formerly introduced poly(acrylate) coated Twister is no longer commercially available, since its applicability and robustness were limited (David et al. 2019). In order to overcome the limitations of polydimethylsiloxane phase, that reduces its use to nonpolar analytes, new coating materials are being developed, so widening the applicability of stir bar sorptive extraction. This interest is catalyzed in part by the need to develop methods for more polar emerging pollutants, such as polar pesticides. These novel materials include carbon adsorbents, molecularly imprinted polymers, sol–gel prepared coatings, restricted access materials, ionic liquids, microporous monoliths and dual phase materials (Abdulra'uf and Tan 2014). Unfortunately, most of the new coating materials can only be used in combination with solvent desorption, which limits the sensitivity of the method since only a fraction of the extract can be analyzed by gas chromatography or liquid chromatography. Large volume injection can partly compensate for this loss.

Recently, Benedé et al. (2014) introduced the use of magnetic nanoparticles coated dynamically with a magnetic stir bar, this technique being termed stir bar sorptive-dispersive microextraction. It combines the principles and benefits of stir bar sorptive extraction and dispersive solid-phase microextraction based on magnetic nanoparticles. At high stirring rate magnetic nanoparticles are dispersed into the sample solution (or into the desorbing solvent) and return to the magnetic bar when the stirring is stopped. Stir bar sorptive-dispersive microextraction with magnetically modified graphene (G-Fe_3O_4) as the sorbent was applied in isolation of seven model pesticides from water samples (boscalid, chlorpyrifos, deltamethrin, dimethenamid-P, dimoxystrobin, metazachlor and tebuconazol) (Madej et al. 2019). The developed method resulted more convenient than magnetic solid-phase extraction, performed in analogous conditions, in terms of sorbent collection and effective mixing of larger sample volumes. The multiclass pesticides analyzed could be detected in concentration of several nanograms per milliliter. Molecularly imprinted stir bars based upon the entrapment of modified magnetic nanoparticles within an imprinted polymer monolith have also been proposed for the stir bar sorptive extraction of triazines in soil sample extracts (Díaz-Álvarez et al. 2016). Although low recoveries were obtained (2.4 to 8.7%), the high selectivity provided by the new molecularly imprinted stir bars allowed reaching detection limits below 7.5 ng g^{-1} by liquid chromatography coupled to UV detection.

In the last decade, multiresidue methods using stir bar sorptive extraction have been described for pesticides, together with endocrine disruptors and other priority pollutants, either with thermal desorption combined with gas chromatography-mass spectrometry (Camino-Sánchez et al. 2012) or liquid desorption combined with liquid chromatography-mass spectrometry (Margoum et al. 2013) and gas chromatography-mass spectrometry (Camino-Sánchez et al. 2012). Recently, Lerch et al. (2018) developed a fully validated method for the analysis of pesticides and other priority pollutants in water samples at ng L^{-1} to sub-ng L^{-1} levels, according to the European Union Water Framework Directives (European Union 2008; European Union 2013; European Union 2015).

By comparing solid-phase microextraction and stir bar sorptive extraction, apart from other advantages, we can conclude that these solventless techniques combine simultaneously extraction and concentration of the analytes in a single step, present easy and fast manipulation, require low sample volume, allow reutilization, can operate overnight, do not present the breakthrough phenomena, are cost-effective, can be easily combined with modern analytical instrumentation and have demonstrated their applicability to a wide range of samples (Nogueira 2015). Although solid-phase microextraction has lower capacity due the limited amount of sorbent phase, it is definitely more appropriate for analysis of semi-volatile to volatile analytes than stir bar sorptive extraction when the headspace mode followed by gas chromatography is used.

2.4 Gel permeation chromatography

Gel permeation chromatography is an efficient technique that was first used in 1970s for extraction and cleanup of pesticides (Holding 1984). The gel permeation chromatography separation mechanism is based on the principle of size exclusion where larger molecules are eluted from the stationary phase (gel), followed by smaller molecules. Gel permeation chromatography columns are packed with a cross-linked polymer material that is very porous, so that small molecules can get into the pores and are thus retained for longer periods of time on the column, whereas large molecules cannot and therefore pass through the column very quickly. Cross-linked dextrans such as Sephadex or agarose are commonly used materials. Because of the robustness, rapidity, convenience, and cleanup efficiency, gel permeation chromatography has been used as a universal technique for the pretreatment of complex samples before multiresidue pesticide analysis (Huang et al. 2007; Cajka et al. 2008), and especially to purify fat-rich extracts, such as those coming from olive oil (Guardia-Rubio et al. 2006), milk (Zheng et al. 2014), avocado (Fernández Moreno et al. 2006), or pork and lamb meat (Garrido Frenich et al. 2006). Lipids, which are often co-extracted along with pesticides, may jam in the injector and at the top of the column of gas chromatography. However, lipids are too big and cannot go through the pores of the gel, so that they are eluted first from the column. Different mobile phases can be used for the gel permeation chromatography cleanup: ethyl acetate-cyclohexane (Cajka et al. 2008) or acetone-cyclohexane and hexane-ethyl acetate (Huang et al. 2007).

The analysis of pesticides in oil samples by gas chromatography requires a complete removal of the high molecular weight fat components to lengthen the life of the columns and keep the chromatographic system working properly. Gel permeation chromatography has demonstrated to be a very useful technique to separate the main components of oils (triglycerides) from the low molecular weight of pesticides, being one of the more widely spread techniques (Sánchez et al. 2006; Garrido Frenich et al. 2007). It is generally used after a preliminary solvent partitioning with acetonitrile for the subsequent gas chromatography analysis (Guardia-Rubio et al. 2006). However, there are methods based on direct extraction and cleanup of pesticides from olive oil without a liquid-liquid partition step, using only gel permeation chromatography (Patel et al. 2005). In most cases, the recoveries in gel permeation chromatography are satisfactory and it is applicable to both polar and nonpolar pesticides within the same injection on a fully automated system. A drawback of this technique is the partial overlapping between the pesticide fraction and the components of the matrix (mainly triglycerides), which results in loss of some nonpolar pesticides such as bromopropylate, phenotrin and acrinatrin (Hakme et al. 2018). Therefore, an additional cleanup step is usually included after gel permeation chromatography before chromatographic analysis, for example by solid-phase extraction (Huang et al. 2007). Other drawbacks of gel permeation chromatography are the use of large volumes of organic toxic solvents, the requirement of an additional instrumentation, and that it is time-consuming.

2.5 Conclusions and perspectives

In most analytical methods, the complexity of sample and/or the concentration and nature of analyte(s) make the sample treatment an unavoidable step, so that sample preparation remains the weakest and time-determining stage of the analysis. In many cases, extraction and cleanup techniques are labor intensive, involve the use of organic solvents, energy, and most of them are hazardous to both, laboratory workers and the environment. The particular case of solid samples usually requires, especially for trace analysis, the use of an extraction process to dissolve the target analyte(s) in an aqueous or organic solvent solution previous to analyte pre-concentration.

In the last years, improvements in sample preparation techniques are the result of modifying existing techniques and developing new techniques, always with the aim of saving time and reducing consumption of chemicals and waste generation, and thus to improve overall process performance. High efficacy extraction approaches for solid samples have been developed, such as matrix solid-phase dispersion, microwave-assisted extraction, pressurized liquid extraction, and supercritical fluid extraction. Nevertheless, some of these techniques usually involve a treatment at high temperature and pressure to improve the extraction yield with reduced time and solvent consumption. A special attention deserves the use of headspace extraction for analysis of volatile compounds from solid samples, which is solvent-free, carried out at moderate temperature, and can be combined with solid-phase microextraction for significantly improving extraction efficacy. All these techniques have grown in their maturity with increased applications to pesticide residue analysis in food and environmental samples.

Regarding liquid or dissolved samples, the miniaturization of liquid-liquid extraction has resulted in more efficient extraction techniques with solvent and time savings. Single-drop microextraction, hollow-fiber membrane liquid-phase microextraction, and dispersive liquid-liquid microextraction offer green alternatives to solve problems of sensitivity and/or selectivity of methods to be applied directly to analyze complex samples. Moreover, the use of alternative extractants like ionic liquids, with high solvation properties and versatility, has been explored as potential candidates to replace conventional solvents in a green perspective. As a consequence, and due to the advantageous features they present compared to conventional techniques, currently liquid-phase microextraction techniques play a very important role in sample preparation for analysis, and specifically in pesticide analysis. This is evident from the relatively large number of publications in this regard in recent years.

Other strategies based on the miniaturization of solid-phase extraction, such as solid-phase microextraction and stir bar sorptive extraction have been developed in the last years to reduce substantially sample and solvent consumption. The use of new solid sorbents, such as molecularly imprinted polymers or carbon nanotubes has allowed the development of high selective extraction methods and contributed to reduce the number of steps of analytical procedures. On the other hand, the introduction of magnetic materials has contributed to the development of solid-phase extraction procedures simpler, faster than the conventional methods, achieving sorbent separation by the use of a magnet, which reduces time and energy consumption. On the other hand, QuEChERs method has become in one of the sample treatment mostly applied, not only for extraction of pesticides from food samples, but also from environmental matrices, since it allows performing extraction and cleanup in a single step. This is evident from the fact that important international organizations, the AOAC International and the European Committee for Standardization, have approved two different official methods based on method QuEChERs for pesticide analysis.

In the future, it is expected that the development of new techniques as well as all improvements in current sample preparation techniques will be aimed at improving the efficiency of extraction and removal of matrix co-extractives, increasing throughput, and reducing the use of organic solvents. Therefore, as a general rule, these improvements should be directed towards the miniaturization and automation of the analytical process.

References

Abdulra'uf LB, Tan GH (2014) Review of SBSE technique for the analysis of pesticide residues in fruits and vegetables. Chromatographia 77:15–24. doi: 10.1007/s10337-013-2566-8

Ahmad R, Salem NM, Estaitieh H (2010) Occurrence of organochlorine pesticide residues in eggs, chicken and meat in Jordan. Chemosphere 78:667–671. doi: 10.1016/j.chemosphere.2009.12.012

Ahmad W, Al-Sibaai AA, Bashammakh AS, Alwael H, El-Shahawi MS (2015) Recent advances in dispersive liquid-liquid microextraction for pesticide analysis. TrAC Trends Anal Chem 72:181–192. doi: 10.1016/J.TRAC.2015.04.022

Ai J (1997) Headspace solid phase microextraction. Dynamics and quantitative analysis before reaching a partition equilibrium. Anal Chem 69:3260–3266. doi: 10.1021/ac970024x

Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and dispersive solid-phase extraction for the determination of pesticide residues in produce. J AOAC Int 86:412–31. PMID: 12723926.

Andreu V, Picó Y (2004) Determination of pesticides and their degradation products in soil: Critical review and comparison of methods. TrAC Trends Anal Chem 23:772–789. doi: 10.1016/j.trac.2004.07.008

Andreu V, Picó Y (2019) Pressurized liquid extraction of organic contaminants in environmental and food samples. TrAC Trends Anal Chem 118:709–721. doi: 10.1016/j.trac.2019.06.038

AOAC Official Method 2007.01 (2007) Pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulfate gas chromatography/mass spectrometry and liquid chromatography/tandem mass spectrometry first action 2007

Arthur CL, Pawliszyn J (1990) Solid phase microextraction with thermal desorption using fused silica optical fibers. Anal Chem 62:2145–2148. doi: 10.1021/ac00218a019

Asensio-Ramos M, Hernández-Borges J, González-Hernández G, Rodríguez-Delgado MÁ (2012) Hollow-fiber liquid-phase microextraction for the determination of pesticides and metabolites in soils and water samples using HPLC and fluorescence detection. Electrophoresis 33:2184–2191. doi: 10.1002/elps.201200138

Bagheri H, Yamini Y, Safari M, Asiabi H, Karimi M, Heydari A (2016) Simultaneous determination of pyrethroids residues in fruit and vegetable samples via supercritical fluid extraction coupled with magnetic solid phase extraction followed by HPLC-UV. J Supercrit Fluids 107:571–580. doi: 10.1016/j.supflu.2015.07.017

Baltussen E, Sandra P, David F, Cramers C (1999) Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. J Microcolumn Sep 11:737–747. doi: 10.1002/(SICI)1520-667X(1999)11:10<737::AID-MCS7>3.0.CO;2-4

Banerjee K, Oulkar DP, Dasgupta S, Patil SB, Patil SH, Savant R, Adsule PG (2007) Validation and uncertainty analysis of a multi-residue method for pesticides in grapes using ethyl acetate extraction and liquid chromatography–tandem mass spectrometry. J Chromatogr A 1173:98–109. doi: 10.1016/j.chroma.2007.10.013

Barker SA, Long AR, Short CR (1989) Isolation of drug residues from tissues by solid phase dispersion. J Chromatogr A 475:353–361. doi: 10.1016/S0021-9673(01)89689-8

Barriada-Pereira M, González-Castro MJ, Muniategui-Lorenzo S, López-Mahía P, Prada-Rodríguez D (2010) Sample preparation based on matrix solid-phase dispersion and solid-phase extraction cleanup for the determination of organochlorine pesticides in fish. J AOAC Int 93:992–998. PMID: 20629405.

Basheer C, Lee HK, Obbard JP (2002) Determination of organochlorine pesticides in seawater using liquid-phase hollow fibre membrane microextraction and gas chromatography-mass spectrometry. J Chromatogr A 968:191–199. doi: 10.1016/s0021-9673(02)00793-8

Basheer C, Obbard JP, Lee HK (2005) Analysis of persistent organic pollutants in marine sediments using a novel microwave assisted solvent extraction and liquid-phase microextraction technique. J Chromatogr A 1068:221–228. doi: 10.1016/j.chroma.2005.01.099

Basheer C, Suresh V, Renu R, Lee HK (2004) Development and application of polymer-coated hollow fiber membrane microextraction to the determination of organochlorine pesticides in water. J Chromatogr A 1033:213–220. doi: 10.1016/j.chroma.2004.01.050

Beltran J, López FJ, Hernández F (2000) Solid-phase microextraction in pesticide residue analysis. J. Chromatogr A 885:389–404. doi: 10.1016/S0021-9673(00)00142-4

Benedé JL, Chisvert A, Giokas DL, Salvador A (2014) Development of stir bar sorptive-dispersive microextraction mediated by magnetic nanoparticles and its analytical application to the determination of hydrophobic organic compounds in aqueous media. J Chromatogr A 1362:25–33. doi: 10.1016/j.chroma.2014.08.024

Berijani S, Assadi Y, Anbia M, Milani Hosseini M-R, Aghaee E (2006) Dispersive liquid–liquid microextraction combined with gas chromatography-flame photometric detection: Very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water. J Chromatogr A 1123:1–9. doi: 10.1016/j.chroma.2006.05.010

Beyer A, Biziuk M (2008) Applications of sample preparation techniques in the analysis of pesticides and PCBs in food. Food Chem 108:669–680. doi: 10.1016/j.foodchem.2007.11.024

Binellas CS, Stalikas CD (2015) Magnetic octadecyl-based matrix solid-phase dispersion coupled with gas chromatography with mass spectrometry in a proof-of-concept determination of multi-class pesticide residues in carrots. J Sep Sci 38:3575–3581. doi: 10.1002/jssc.201500519

Blasco C, Vazquez-Roig P, Onghena M, Masia A, Picó Y (2011) Analysis of insecticides in honey by liquid chromatography-ion trap-mass spectrometry: Comparison of different extraction procedures. J Chromatogr A 1218:4892–4901. doi: 10.1016/j.chroma.2011.02.045

Bolaños PP, Romero-González R, Frenich AG, Vidal JLM (2008) Application of hollow fibre liquid phase microextraction for the multiresidue determination of pesticides in alcoholic beverages by ultra-high pressure liquid chromatography coupled to tandem mass spectrometry. J Chromatogr A 1208:16–24. doi: 10.1016/j.chroma.2008.08.059

Bratkowska D, Fontanals N, Borrull F, Cormack PAG, Sherrington DC, Marcé RM (2010) Hydrophilic hypercrosslinked polymeric sorbents for the solid-phase extraction of polar contaminants from water. J Chromatogr A 1217:3238–3243. doi: 10.1016/j.chroma.2009.08.091

Cabras P, Angioni A, Garau VL, Pirisi FM, Cabitza F, Pala M, Farris GA (2001) Fenhexamid residues in grapes and wine. Food Addit Contam 18:625–629. doi: 10.1080/02652030120571

Cajka T, Hajslova J, Lacina O, Mastovska K, Lehotay SJ (2008) Rapid analysis of multiple pesticide residues in fruit-based baby food using programmed temperature vaporiser injection-low-pressure gas chromatography-high-resolution time-of-flight mass spectrometry. J Chromatogr A 1186:281–294. doi: 10.1016/j.chroma.2007.12.009

Camino-Sánchez FJ, Rodríguez-Gómez R, Zafra-Gómez A, Santos-Fandila A, Vílchez JL (2014) Stir bar sorptive extraction: Recent applications, limitations and future trends. Talanta 130:388–399. doi: 10.1016/j.talanta.2014.07.022

Camino-Sánchez FJ, Zafra-Gómez A, Cantarero-Malagón S, Vílchez JL (2012) Validation of a method for the analysis of 77 priority persistent organic pollutants in river water by stir bar sorptive extraction in compliance with the European Water Framework Directive. Talanta 89:322–334. doi: 10.1016/j.talanta.2011.12.037

Campillo N, Viñas P, Aguinaga N, Férez G, Hernández-Córdoba M (2010) Stir bar sorptive extraction coupled to liquid chromatography for the analysis of strobilurin fungicides in fruit samples. J Chromatogr A 1217:4529–4534. doi: 10.1016/j.chroma.2010.05.006

Capriotti AL, Cavaliere C, Laganà A, Piovesana S, Samperi R (2013) Recent trends in matrix solid-phase dispersion. TrAC Trends Anal Chem 43:53–66. doi: 10.1016/j.trac.2012.09.021

Carvalho PN, Rodrigues PNR, Alves F, Evangelista R, Basto MCP, Vasconcelos MTSD (2008) An expeditious method for the determination of organochlorine pesticides residues in estuarine sediments using microwave assisted pre-extraction and automated headspace solid-phase microextraction coupled to gas chromatography–mass spectrometry. Talanta 76:1124–1129. doi: 10.1016/j.talanta.2008.05.035

Celeiro M, Llompart M, Lamas JP, Lores M, Garcia-Jares C, Dagnac T (2014) Determination of fungicides in white grape bagasse by pressurized liquid extraction and gas chromatography tandem mass spectrometry. J Chromatogr A 1343:18–25. doi: 10.1016/j.chroma.2014.03.057

Cerqueira MBR, Caldas SS, Primel EG (2014) New sorbent in the dispersive solid phase extraction step of quick, easy, cheap, effective, rugged, and safe for the extraction of organic contaminants in drinking water treatment sludge. J Chromatogr A 1336:10–22. doi: 10.1016/j.chroma.2014.02.002

Chatzimitakos TG, Anderson JL, Stalikas CD (2018) Matrix solid-phase dispersion based on magnetic ionic liquids: An alternative sample preparation approach for the extraction of pesticides from vegetables. J Chromatogr A 1581–1582:168–172. doi: 10.1016/j.chroma.2018.11.008

Chaves AR, Silva SM, Queiroz RHC, Lanças FM, Queiroz MEC (2007) Stir bar sorptive extraction and liquid chromatography with UV detection for determination of antidepressants in plasma samples. J Chromatogr B 850:295–302. doi: 10.1016/j.jchromb.2006.11.042

Chee KK, Wong MK, Lee HK (1996) Determination of organochlorine pesticides in water by membranous solid-phase extraction, and in sediment by microwave-assisted solvent extraction with gas chromatography and electron-capture and mass spectrometric detection. J Chromatogr A 736:211–218. doi: 10.1016/0021-9673(95)01354-7

Chen C-C, Melwanki MB, Huang S-D (2006) Liquid–liquid–liquid microextraction with automated movement of the acceptor and the donor phase for the extraction of phenoxyacetic acids prior to liquid chromatography detection. J Chromatogr A 1104:33–39. doi: 10.1016/j.chroma.2005.11.122

Chen P-S, Huang S-D (2006) Determination of ethoprop, diazinon, disulfoton and fenthion using dynamic hollow fiber-protected liquid-phase microextraction coupled with gas chromatography–mass spectrometry. Talanta 69:669–675. doi: 10.1016/j.talanta.2005.10.042

Cheng Z, Dong F, Xu J, Liu X, Wu X, Chen Z, Pan X, Zheng Y (2016) Atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry for simultaneous determination of fifteen organochlorine pesticides in soil and water. J Chromatogr A 1435:115–124. doi: 10.1016/j.chroma.2016.01.025

Choi M, Lee I-S, Jung R-H (2016) Rapid determination of organochlorine pesticides in fish using selective pressurized liquid extraction and gas chromatography–mass spectrometry. Food Chem 205:1–8. doi: 10.1016/j.foodchem.2016.02.156

Clark AE, Yoon S, Sheesley RJ, Usenko S (2015) Pressurized liquid extraction technique for the analysis of pesticides, PCBs, PBDEs, OPEs, PAHs, alkanes, hopanes, and steranes in atmospheric particulate matter. Chemosphere 137:33–44. doi: 10.1016/j.chemosphere.2015.04.051

Codex Alimentarius. Pesticides residues in food online database. Available on: http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/en/ (accessed on September 2019)

Cunha SC, Lehotay SJ, Mastovska K, Fernandes JO, Beatriz M, Oliveira PP (2007) Evaluation of the QuEChERS sample preparation approach for the analysis of pesticide residues in olives. J Sep Sci 30:620–632. doi: 10.1002/jssc.200600410

Da Silva Souza NR, Navickiene S (2019) Multiresidue determination of carbamate, organophosphate, neonicotinoid and triazole pesticides in roasted coffee using ultrasonic solvent extraction and liquid chromatography-tandem mass spectrometry. J AOAC Int 102:33–37. doi: 10.5740/jaoacint.18-0294

David F, Ochiai N, Sandra P (2019) Two decades of stir bar sorptive extraction: A retrospective and future outlook. TrAC Trends Anal Chem 112:102–111. doi: 10.1016/j.trac.2018.12.006

De Grazia S, Gionfriddo E, Pawliszyn J (2017) A new and efficient solid phase microextraction approach for analysis of high fat content food samples using a matrix-compatible coating. Talanta 167:754–760. doi: 10.1016/j.talanta.2017.01.064

Dias J V., Cutillas V, Lozano A, Pizzutti IR, Fernández-Alba AR (2016) Determination of pesticides in edible oils by liquid chromatography-tandem mass spectrometry employing new generation materials for dispersive solid phase extraction clean-up. J Chromatogr A 1462:8–18. doi: 10.1016/j.chroma.2016.07.072

Díaz-Álvarez M, Turiel E, Martín-Esteban A (2016) Molecularly imprinted polymer monolith containing magnetic nanoparticles for the stir-bar sorptive extraction of triazines from environmental soil samples. J Chromatogr A 1469:1–7. doi: 10.1016/j.chroma.2016.09.051

Doong R, Lee C (1999) Determination of organochlorine pesticide residues in foods using solid-phase extraction clean-up cartridges. Analyst 124:1287–1289. doi: 10.1039/a902722j

Du D, Wang M, Zhang J, Cai J, Tu H, Zhang A (2008) Application of multiwalled carbon nanotubes for solid-phase extraction of organophosphate pesticide. Electrochem Commun 10:85–89. doi: 10.1016/j.elecom.2007.11.005

Ebrahimi M, Es‘haghi Z, Samadi F, Hosseini M-S (2011) Ionic liquid mediated sol–gel sorbents for hollow fiber solid-phase microextraction of pesticide residues in water and hair samples. J Chromatogr A 1218:8313–8321. doi: 10.1016/j.chroma.2011.09.058

Eisert R, Pawliszyn J (1997) Automated in-tube solid-phase microextraction coupled to high-performance liquid chromatography. Anal Chem 69:3140–3147. doi: 10.1021/ac970319a

El-Sheikh AH, Sweileh JA, Al-Degs YS, Insisi AA, Al-Rabady N (2008) Critical evaluation and comparison of enrichment efficiency of multi-walled carbon nanotubes, C_{18} silica and activated carbon towards some pesticides from environmental waters. Talanta 74:1675–1680. doi: 10.1016/j.talanta.2007.09.005

European Committee for Standardization (CEN) Standard Method EN 15662:2008 (2008) Multimethod for the determination of pesticide residues using GC- and LC-based analysis following acetonitrile extraction/partitioning and clean-up by dispersive SPE - Modular QuEChERS-method

European Food Safety Authority (2018) The 2016 European Union report on pesticide residues in food. EFSA J 16:5348. doi: 10.2903/j.efsa.2018.5348

European Union (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Off J Eur Union L 327/1.

European Union (2005) Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC. Off J Eur Union L 70/1.

European Union (2008) Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC. Off J Eur Union L 348/84.

European Union (2013) Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Off J Eur Union L 226/1.

European Union (2015) Decision 2015/495. Commission Implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. Off J Eur Union L 78/40.

Falqui-Cao C, Wang Z, Urruty L, Pommier JJ, Montury M (2001) Focused microwave assistance for extracting some pesticide residues from strawberries into water before their determination by SPME/HPLC/DAD. J Agric Food Chem 49:5092–5097. doi: 10.1021/jf010519u

Fang G, Min G, He J, Zhang C, Qian K, Wang S (2009) Multiwalled carbon nanotubes as matrix solid-phase dispersion extraction absorbents to determine 31 pesticides in agriculture samples by gas chromatography-mass spectrometry. J Agric Food Chem 57:3040–3045. doi: 10.1021/jf803913q

Farajzadeh MA, Feriduni B, Mogaddam MRA (2014) Extraction and enrichment of triazole and triazine pesticides from honey using air-assisted liquid-liquid microextraction. J Food Sci 79:H2140–H2148. doi: 10.1111/1750-

3841.12597

Farajzadeh MA, Feriduni B, Mogaddam MRA (2015) Determination of triazole pesticide residues in edible oils using air-assisted liquid-liquid microextraction followed by gas chromatography with flame ionization detection. J Sep Sci 38:1002–1009. doi: 10.1002/jssc.201400818

Farajzadeh MA, Khoshmaram L (2013) Air-assisted liquid-liquid microextraction-gas chromatography-flame ionisation detection: A fast and simple method for the assessment of triazole pesticides residues in surface water, cucumber, tomato and grape juices samples. Food Chem 141:1881–1887. doi: 10.1016/j.foodchem.2013.05.088

Farajzadeh MA, Mogaddam MRA (2012) Air-assisted liquid-liquid microextraction method as a novel microextraction technique; Application in extraction and preconcentration of phthalate esters in aqueous sample followed by gas chromatography-flame ionization detection. Anal Chim Acta 728:31–38. doi: 10.1016/j.aca.2012.03.031

Farajzadeh MA, Seyedi SE, Shalamzari MS, Bamorowat M (2009) Dispersive liquid-liquid microextraction using extraction solvent lighter than water. J Sep Sci 32:3191–3200. doi: 10.1002/jssc.200900109

Farajzadeh MA, Sohrabi H, Mohebbi A (2019) Combination of modified QuEChERS extraction method and dispersive liquid–liquid microextraction as an efficient sample preparation approach for extraction and preconcentration of pesticides from fruit and vegetable samples. Food Anal Methods 12:534–543. doi: 10.1007/s12161-018-1384-x

Fernandez-Alba AR, Valverde A, Agüera A, Contreras M (1994) Gas chromatographic determination of organochlorine and pyrethroid pesticides of horticultural concern. J Chromatogr A 686:263–274. doi: 10.1016/0021-9673(94)00735-7

Fernandez-Alvarez M, Llompart M, Garcia-Jares C, Dagnac T, Lores M (2009) Investigation of the photochemical behaviour of pyrethroids lacking the cyclopropane ring by photo-solid-phase microextraction and gas chromatography/mass spectrometry. Rapid Commun Mass Spectrom 23:3673–3687. doi: 10.1002/rcm.4301

Fernandez-Alvarez M, Llompart M, Lamas JP, Lores M, Garcia-Jares C, Cela R, Dagnac T (2008) Simultaneous determination of traces of pyrethroids, organochlorines and other main plant protection agents in agricultural soils by headspace solid-phase microextraction-gas chromatography. J Chromatogr A 1188:154–163. doi: 10.1016/j.chroma.2008.02.080

Fernández Moreno JL, Arrebola Liébanas FJ, Garrido Frenich A, Martínez Vidal JL (2006) Evaluation of different sample treatments for determining pesticide residues in fat vegetable matrices like avocado by low-pressure gas chromatography-tandem mass spectrometry. J Chromatogr A 1111:97–105. doi: 10.1016/j.chroma.2006.01.108

Fiddler W, Pensabene JW, Gates RA, Donoghue DJ (1999) Supercritical fluid extraction of organochlorine pesticides in eggs. J Agric Food Chem 47:206–211. doi: 10.1021/jf980436m

Fillion J, Sauvé F, Selwyn J (2000) Multiresidue method for the determination of residues of 251 pesticides in fruits and vegetables by gas chromatography/mass spectrometry and liquid chromatography with fluorescence detection. J AOAC Int 83:698–713. PMID: 10868594

Font N, Hernández F, Hogendoorn E., Baumann R., van Zoonen P (1998) Microwave-assisted solvent extraction and reversed-phase liquid chromatography–UV detection for screening soils for sulfonylurea herbicides. J Chromatogr A 798:179–186. doi: 10.1016/S0021-9673(97)01194-1

Fontana AR, Camargo A, Martinez LD, Altamirano JC (2011) Dispersive solid-phase extraction as a simplified clean-up technique for biological sample extracts. Determination of polybrominated diphenyl ethers by gas chromatography–tandem mass spectrometry. J Chromatogr A 1218:2490–2496. doi: 10.1016/j.chroma.2011.02.058

Fontanals N, Marcé RM, Borrull F (2005) New hydrophilic materials for solid-phase extraction. TrAC Trends Anal Chem 24:394–406. doi: 10.1016/j.trac.2005.01.012

Fuentes E, Báez ME, Díaz J (2009) Microwave-assisted extraction at atmospheric pressure coupled to different clean-up methods for the determination of organophosphorus pesticides in olive and avocado oil. J Chromatogr A 1216:8859–8866. doi: 10.1016/j.chroma.2009.10.082

Garbi A, Sakkas V, Fiamegos YC, Stalikas CD, Albanis T (2010) Sensitive determination of pesticides residues in wine samples with the aid of single-drop microextraction and response surface methodology. Talanta 82:1286–1291. doi: 10.1016/j.talanta.2010.06.046

Garcia R, Carreiro EP, Nunes J, Da Silva MG, Freitas AMC, Burke AJ, Cabrita MJ (2016) Dual-layer solid-phase extraction based on molecular imprinting technology: Seeking a route to enhance selectivity for trace analysis of pesticide residues in olive oil. Electrophoresis 37:1916–1922. doi: 10.1002/elps.201600073

Garrido Frenich A, Fernández Moreno JL, Martínez Vidal JL, Arrebola Liébanas FJ (2007) Application of gas chromatography coupled to triple quadrupole mass spectrometry for the multiresidue analysis of pesticides in olive oil. J Agric Food Chem 55:8346–8352. doi: 10.1021/jf071615j

Garrido Frenich A, Martínez Vidal JL, Cruz Sicilia AD, González Rodríguez MJ, Plaza Bolaños P (2006) Multiresidue analysis of organochlorine and organophosphorus pesticides in muscle of chicken, pork and lamb by gas chromatography-triple quadrupole mass spectrometry. Anal Chim Acta 558:42–52. doi: 10.1016/j.aca.2005.11.012

Godage NH, Gionfriddo E (2019) A critical outlook on recent developments and applications of matrix compatible coatings for solid phase microextraction. TrAC Trends Anal. Chem. 111:220–228. doi: 10.1016/j.trac.2018.12.019

Gonçalves C, Alpendurada MF (2005) Assessment of pesticide contamination in soil samples from an intensive horticulture area, using ultrasonic extraction and gas chromatography–mass spectrometry. Talanta 65:1179–1189. doi: 10.1016/j.talanta.2004.08.057

Gou Y, Eisert R, Pawliszyn J (2000) Automated in-tube solid-phase microextraction-high-performance liquid chromatography for carbamate pesticide analysis. J Chromatogr A 873:137–147. doi: 10.1016/S0021-9673(99)01125-5

Guan H, Brewer WE, Garris ST, Craft C, Morgan SL (2010) Multiresidue analysis of pesticides in fruits and vegetables using disposable pipette extraction (DPX) and micro-Luke method. J Agric Food Chem 58:5973–5981. doi: 10.1021/jf903448w

Guan W, Li Z, Zhang H, Hong H, Rebeyev N, Ye Y, Ma Y (2013) Amine modified graphene as reversed-dispersive solid phase extraction materials combined with liquid chromatography–tandem mass spectrometry for pesticide multi-residue analysis in oil crops. J Chromatogr A 1286:1–8. doi: 10.1016/j.chroma.2013.02.043

Guardia-Rubio M, Fernández-De Córdova ML, Ayora-Cañada MJ, Ruiz-Medina A (2006) Simplified pesticide multiresidue analysis in virgin olive oil by gas chromatography with thermoionic specific, electron-capture and mass spectrometric detection. J Chromatogr A 1108:231–239. doi: 10.1016/j.chroma.2006.01.006

Guardia Rubio M, Ruiz Medina A, Pascual Reguera MI, Fernández de Córdova ML (2007) Multiresidue analysis of three groups of pesticides in washing waters from olive processing by solid-phase extraction-gas chromatography with electron capture and thermionic specific detection. Microchem J 85:257–264. doi: 10.1016/j.microc.2006.06.005

Hakme E, Lozano A, Ferrer C, Díaz-Galiano FJ, Fernández-Alba AR (2018) Analysis of pesticide residues in olive oil and other vegetable oils. TrAC Trends Anal Chem 100:167–179. doi: 10.1016/j.trac.2017.12.016

Hamed AM, Moreno-González D, Gámiz-Gracia L, García-Campaña AM (2017) Evaluation of a new modified QuEChERS method for the monitoring of carbamate residues in high-fat cheeses by using UHPLC-MS/MS. J Sep Sci 40:488–496. doi: 10.1002/jssc.201600845

Han D, Row KH (2012) Trends in liquid-phase microextraction, and its application to environmental and biological samples. Microchim Acta 76:1–22. doi: 10.1007/s00604-011-0678-0

Han L, Matarrita J, Sapozhnikova Y, Lehotay SJ (2016) Evaluation of a recent product to remove lipids and other matrix co-extractives in the analysis of pesticide residues and environmental contaminants in foods. J Chromatogr A 1449:17–29. doi: 10.1016/j.chroma.2016.04.052

Hanot V, Goscinny S, Deridder M (2015) A simple multi-residue method for the determination of pesticides in fruits and vegetables using a methanolic extraction and ultra-high-performance liquid chromatography-tandem mass spectrometry: Optimization and extension of scope. J Chromatogr A 1384:53–66. doi: 10.1016/j.chroma.2015.01.040

He Z, Wang Y, Wang L, Peng Y, Wang W, Liu X (2017) Determination of 255 pesticides in edible vegetable oils using QuEChERS method and gas chromatography tandem mass spectrometry. Anal Bioanal Chem 409:1017–1030. doi: 10.1007/s00216-016-0016-9

Hercegová A, Dömötörová M, Matisová E (2007) Sample preparation methods in the analysis of pesticide residues in baby food with subsequent chromatographic determination. J Chromatogr A 1153:54–73. doi: 10.1016/j.chroma.2007.01.008

Ho YM, Tsoi YK, Leung KSY (2013) Highly sensitive and selective organophosphate screening in twelve commodities of fruits, vegetables and herbal medicines by dispersive liquid-liquid microextraction. Anal Chim Acta 775:58–66. doi: 10.1016/j.aca.2013.02.043

Holding S. (1984) Gel permeation chromatography. Endeavour 8:17–20. doi: 10.1016/0160-9327(84)90124-8

Homazava N, Gachet Aquillon C, Vermeirssen E, Werner I (2014) Simultaneous multi-residue pesticide analysis in soil samples with ultra-high-performance liquid chromatography–tandem mass spectrometry using QuEChERS and pressurised liquid extraction methods. Int J Environ Anal Chem 94:1085–1099. doi: 10.1080/03067319.2014.954558

Hopper ML (1999) Automated one-step supercritical fluid extraction and clean-up system for the analysis of pesticide residues in fatty matrices. J Chromatogr A 840:93–105. doi: 10.1016/s0021-9673(99)00228-9

Hou L, Lee HK (2004) Determination of pesticides in soil by liquid-phase microextraction and gas chromatography–mass spectrometry. J Chromatogr A 1038:37–42. doi: 10.1016/j.chroma.2004.03.012

Howard AL, Braue C, Taylor LT (1993) Feasibility of thiocarbamate pesticide analysis in apples by supercritical fluid extraction and high-performance liquid chromatography. J Chromatogr Sci 31:323–329. doi: 10.1093/chromsci/31.8.323

Huang Z, Li Y, Chen B, Yao S (2007) Simultaneous determination of 102 pesticide residues in Chinese teas by gas chromatography–mass spectrometry. J Chromatogr B 853:154–162. doi: 10.1016/j.jchromb.2007.03.013

Iijima S (1991) Helical microtubules of graphitic carbon. Nature 354:56–58. doi: 10.1038/354056a0

Janda V, Steenbeke G, Sandra P (1989) Supercritical fluid extraction of s-triazine herbicides from sediment. J Chromatogr A 479:200–205. doi: 10.1016/S0021-9673(01)83334-3

Jia C, Zhu X, Wang J, Zhao E, He M, Chen L, Yu P (2010) Extraction of pesticides in water samples using vortex-assisted liquid–liquid microextraction. J Chromatogr A 1217:5868–5871. doi: 10.1016/j.chroma.2010.07.055

Juan-García A, Font G, Juan C, Picó Y (2010) Pressurised liquid extraction and capillary electrophoresis–mass spectrometry for the analysis of pesticide residues in fruits from Valencian markets, Spain. Food Chem 120:1242–1249. doi: 10.1016/j.foodchem.2009.11.071

Juan-García A, Picó Y, Font G (2005) Capillary electrophoresis for analyzing pesticides in fruits and vegetables using solid-phase extraction and stir-bar sorptive extraction. J Chromatogr A 1073:229–236. doi: 10.1016/j.chroma.2004.09.028

Kaczyński P, Łozowicka B, Perkowski M, Szabuńko J (2017) Multiclass pesticide residue analysis in fish muscle and liver on one-step extraction-cleanup strategy coupled with liquid chromatography tandem mass spectrometry. Ecotoxicol Environ Saf 138:179–189. doi: 10.1016/j.ecoenv.2016.12.040

Khan Z, Kamble N, Bhongale A, Girme M, Bahadur Chauhan V, Banerjee K (2018) Analysis of pesticide residues in tuber crops using pressurised liquid extraction and gas chromatography-tandem mass spectrometry. Food Chem 241:250–257. doi: 10.1016/j.foodchem.2017.08.091

Köck-Schulmeyer M, Olmos M, López de Alda M, Barceló D (2013) Development of a multiresidue method for analysis of pesticides in sediments based on isotope dilution and liquid chromatography-electrospray–tandem mass spectrometry. J Chromatogr A 1305:176–187. doi: 10.1016/j.chroma.2013.07.036

Kokosa JM (2015) Recent trends in using single-drop microextraction and related techniques in green analytical methods. TrAC Trends Anal Chem 71:194–204. doi: 10.1016/j.trac.2015.04.019

Lambropoulou DA, Albanis TA (2007) Liquid-phase micro-extraction techniques in pesticide residue analysis. J Biochem Biophys Methods 70:195–228. doi: 10.1016/j.jbbm.2006.10.004

Lambropoulou DA, Albanis TA (2005) Application of hollow fiber liquid phase microextraction for the determination of insecticides in water. J Chromatogr A 1072:55–61. doi: 10.1016/j.chroma.2004.11.076

Lambropoulou DA, Konstantinou IK, Albanis TA (2006) Coupling of headspace solid phase microextraction with ultrasonic extraction for the determination of chlorinated pesticides in bird livers using gas chromatography. Anal Chim Acta 573–574:223–230. doi: 10.1016/j.aca.2006.05.048

Lashgari M, Yamini Y (2019) An overview of the most common lab-made coating materials in solid phase microextraction. Talanta 191:283–306. doi: 10.1016/j.talanta.2018.08.077

LeDoux M (2011) Analytical methods applied to the determination of pesticide residues in foods of animal origin. A review of the past two decades. J Chromatogr A 1218:1021–1036. doi: 10.1016/j.chroma.2010.12.097

Lee J, Lee HK, Rasmussen KE, Pedersen-Bjergaard S (2008) Environmental and bioanalytical applications of hollow fiber membrane liquid-phase microextraction: A review. Anal Chim Acta 624:253–268. doi: 10.1016/j.aca.2008.06.050

Lehotay SJ, de Kok A, Hiemstra M, Van Bodegraven P (2005a) Validation of a fast and easy method for the determination of residues from 229 pesticides in fruits and vegetables using gas and liquid chromatography and mass spectrometric detection. J AOAC Int 88:595–614. PMID: 15859089

Lehotay SJ, Eller KI (1995) Development of a method of analysis for 46 pesticides in fruits and vegetables by supercritical fluid extraction and gas chromatography/ion trap mass spectrometry. J AOAC Int 78:821–830. PMID: 7756898

Lehotay SJ, Lightfield AR, Harman-Fetcho JA, Donoghue DJ (2001) Analysis of pesticide residues in eggs by direct sample introduction/gas chromatography/tandem mass spectrometry. J Agric Food Chem 49:4589–4596. doi: 10.1021/jf0104836

Lehotay SJ, Mastovská K, Yun SJ (2005b) Evaluation of two fast and easy methods for pesticide residue analysis in fatty food matrixes. J AOAC Int 88:630–638. PMID: 15859091

León V., Álvarez B, Cobollo M., Muñoz S, Valor I (2003) Analysis of 35 priority semivolatile compounds in water by stir bar sorptive extraction–thermal desorption–gas chromatography–mass spectrometry: I. Method optimisation. J Chromatogr A 999:91–101. doi: 10.1016/S0021-9673(03)00600-9

Leong MI, Huang S Da (2009) Dispersive liquid-liquid microextraction method based on solidification of floating organic drop for extraction of organochlorine pesticides in water samples. J Chromatogr A 1216:7645–7650. doi: 10.1016/j.chroma.2009.09.004

Lerch TO, Zboron J, Brady K AJ-L (2018) Highly sensitive determination of contaminants in surface water in the context of the EU Water Framework Directive using stir bar sorptive extraction (SBSE) and GC-MS/MS. Gerstel Appl Note No 196. Available on-line at: http://www.gerstel.es/pdf/AppNote-196.pdf (accessed on September 2019).

Li B, Zeng F, Dong Q, Cao Y, Fan H, Deng C (2012) Rapid determination method for 12 pyrethroid pesticide residues in tea by stir bar sorptive extraction-thermal desorption-gas chromatography. Phys Procedia 25:1776-1780. doi: 10.1016/j.phpro.2012.03.310

Liang P, Wang F, Wan Q (2013) Ionic liquid-based ultrasound-assisted emulsification microextraction coupled with high performance liquid chromatography for the determination of four fungicides in environmental water samples. Talanta 105:57–62. doi: 10.1016/j.talanta.2012.11.065

Liu J, Jiang G, Chi Y, Cai Y, Zhou Q, Hu J-T (2003) Use of ionic liquids for liquid-phase microextraction of polycyclic aromatic hydrocarbons. Anal Chem 75:5870–5876. doi: 10.1021/ac034506m

Liu W, Hu Y, Zhao J, Xu Y, Guan Y (2005) Determination of organophosphorus pesticides in cucumber and potato by stir bar sorptive extraction. J Chromatogr A 1095:1–7. doi: 10.1016/j.chroma.2005.07.107

Liu Z, Liu W, Rao H, Feng T, Li C, Wang C, Wang Z (2012) Determination of some carbamate pesticides in watermelon and tomato samples by dispersive liquid-liquid microextraction combined with high performance liquid chromatography. Int J Environ Anal Chem 92:571–581. doi: 10.1080/03067311003628638

Liu ZM, Zang XH, Liu WH, Wang C, Wang Z (2009) Novel method for the determination of five carbamate pesticides in water samples by dispersive liquid-liquid microextraction combined with high performance liquid chromatography. Chinese Chem Lett 20:213–216. doi: 10.1016/j.cclet.2008.10.047

López-Feria S, Cárdenas S, Valcárcel M (2009) One step carbon nanotubes-based solid-phase extraction for the gas chromatographic–mass spectrometric multiclass pesticide control in virgin olive oils. J Chromatogr A 1216:7346–7350. doi: 10.1016/j.chroma.2009.02.060

Lozano A, Rajski Ł, Uclés S, Belmonte-Valles N, Mezcua M, Fernández-Alba AR (2014) Evaluation of zirconium dioxide-based sorbents to decrease the matrix effect in avocado and almond multiresidue pesticide analysis followed by gas chromatography tandem mass spectrometry. Talanta 118:68–83. doi: 10.1016/j.talanta.2013.09.053

Łozowicka B, Jankowska M, Kaczyński P (2012) Pesticide residues in *Brassica* vegetables and exposure assessment of consumers. Food Control 25:561–575. doi: 10.1016/j.foodcont.2011.11.017

Łozowicka B, Rutkowska E, Jankowska M (2017) Influence of QuEChERS modifications on recovery and matrix effect during the multi-residue pesticide analysis in soil by GC/MS/MS and GC/ECD/NPD. Environ Sci Pollut Res 24:7124–7138. doi: 10.1007/s11356-016-8334-1

Luque de Castro MD, Priego-Capote F (2010) Soxhlet extraction: Past and present panacea. J Chromatogr A 1217:2383–2389. doi: 10.1016/j.chroma.2009.11.027

Lüthje K, Hyötyläinen T, Rautiainen-Rämä M, Riekkola M-L (2005) Pressurised hot water extraction-microporous membrane liquid-liquid extraction coupled on-line with gas chromatography-mass spectrometry in the analysis of pesticides in grapes. Analyst 130:52–58. doi: 10.1039/b409276g

Madej K, Jonda A, Borcuch A, Piekoszewski W, Chmielarz L, Gil B (2019) A novel stir bar sorptive-dispersive microextraction in combination with magnetically modified graphene for isolation of seven pesticides from water samples. Microchem J 147:962–971. doi: 10.1016/j.microc.2019.04.002

Manav ÖG, Dinç-Zor Ş, Alpdoğan G (2019) Optimization of a modified QuEChERS method by means of experimental design for multiresidue determination of pesticides in milk and dairy products by GC–MS. Microchem J 144:124–129. doi: 10.1016/j.microc.2018.08.056

Margoum C, Guillemain C, Yang X, Coquery M (2013) Stir bar sorptive extraction coupled to liquid chromatography-tandem mass spectrometry for the determination of pesticides in water samples: Method validation and measurement uncertainty. Talanta 116:1–7. doi: 10.1016/j.talanta.2013.04.066

Masiá A, Vásquez K, Campo J, Picó Y (2015) Assessment of two extraction methods to determine pesticides in soils, sediments and sludges. Application to the Túria River Basin. J Chromatogr A 1378:19–31. doi: 10.1016/j.chroma.2014.11.079

Menezes HC, Paulo BP, Paiva MJN, Cardeal ZL (2016) A simple and quick method for the determination of pesticides in environmental water by HF-LPME-GC/MS. J Anal Methods Chem 2016:7058709. doi: 10.1155/2016/7058709

Merdassa Y, Liu J, Megersa N (2013) Development of a one-step microwave-assisted extraction method for simultaneous determination of organophosphorus pesticides and fungicides in soils by gas chromatography–mass spectrometry. Talanta 114:227–234. doi: 10.1016/j.talanta.2013.04.035

Mirabelli MF, Gionfriddo E, Pawliszyn J, Zenobi R (2018) A quantitative approach for pesticide analysis in grape juice by direct interfacing of a matrix compatible SPME phase to dielectric barrier discharge ionization-mass spectrometry. Analyst 143:891–899. doi: 10.1039/c7an01663h

Moinfar S, Hosseini M-RM (2009) Development of dispersive liquid–liquid microextraction method for the analysis of organophosphorus pesticides in tea. J Hazard Mater 169:907–911. doi: 10.1016/j.jhazmat.2009.04.030

Mol HGJ, Rooseboom A, van Dam R, Roding M, Arondeus K, Sunarto S (2007) Modification and re-validation of the ethyl acetate-based multi-residue method for pesticides in produce. Anal Bioanal Chem 389:1715–1754. doi: 10.1007/s00216-007-1357-1

Moreno-González D, Huertas-Pérez JF, García-Campaña AM, Gámiz-Gracia L (2014) Determination of carbamates in edible vegetable oils by ultra-high performance liquid chromatography-tandem mass spectrometry using a new clean-up based on zirconia for QuEChERS methodology. Talanta 128:299–304. doi: 10.1016/j.talanta.2014.04.045

Moreno-González R, León VM (2017) Presence and distribution of current-use pesticides in surface marine sediments from a Mediterranean coastal lagoon (SE Spain). Environ Sci Pollut Res 24:8033–8048. doi: 10.1007/s11356-017-8456-0

Moreno DV, Ferrera ZS, Rodríguez JJS (2007) SPME and SPE comparative study for coupling with microwave-assisted micellar extraction in the analysis of organochlorine pesticides residues in seaweed samples. Microchem J 87:139–146. doi: 10.1016/j.microc.2007.07.002

Nemoto S, Sasaki K, Toyoda M, Saito Y (1997) Effect of extraction conditions and modifiers on the supercritical fluid extraction of 88 pesticides. J Chromatogr Sci 35:467–477. doi: 10.1093/chromsci/35.10.467

Neuwirthová N, Trojan M, Svobodová M, Vašíčková J, Šimek Z, Hofman J, Bielská L (2019) Pesticide residues remaining in soils from previous growing season(s) - Can they accumulate in non-target organisms and contaminate the food web? Sci Total Environ 646:1056–1062. doi: 10.1016/j.scitotenv.2018.07.357

Nguyen TD, Lee MH, Lee GH (2010) Rapid determination of 95 pesticides in soybean oil using liquid–liquid extraction followed by centrifugation, freezing and dispersive solid phase extraction as cleanup steps and gas chromatography with mass spectrometric detection. Microchem J 95:113–119. doi: 10.1016/j.microc.2009.11.009

Nogueira JMF (2015) Stir-bar sorptive extraction: 15 years making sample preparation more environment-friendly. TrAC Trends Anal Chem 71:214-223. doi: 10.1016/j.trac.2015.05.002

Norman KN., Panton SH. (2001) Supercritical fluid extraction and quantitative determination of organophosphorus pesticide residues in wheat and maize using gas chromatography with flame photometric and mass spectrometric detection. J Chromatogr A 907:247–255. doi: 10.1016/S0021-9673(00)01081-5

Ono Y, Yamagami T, Nishina T, Tobino T (2006) Pesticide multiresidue analysis of 303 compounds using supercritical fluid extraction. Anal Sci 22:1473–1476. doi: 10.2116/analsci.22.1473

Pan J, Xia X-X, Liang J (2008) Analysis of pesticide multi-residues in leafy vegetables by ultrasonic solvent extraction and liquid chromatography-tandem mass spectrometry. Ultrason Sonochem 15:25–32. doi: 10.1016/j.ultsonch.2007.06.005

Pano-Farias NS, Ceballos-Magaña SG, Muñiz-Valencia R, Jurado JM, Alcázar Á, Aguayo-Villarreal IA (2017) Direct immersion single drop micro-extraction method for multi-class pesticides analysis in mango using GC–MS. Food Chem 237:30–38. doi: 10.1016/j.foodchem.2017.05.030

Parrilla Vázquez P, Hakme E, Uclés S, Cutillas V, Martínez Galera M, Mughari AR, Fernández-Alba AR (2016) Large multiresidue analysis of pesticides in edible vegetable oils by using efficient solid-phase extraction sorbents based on quick, easy, cheap, effective, rugged and safe methodology followed by gas chromatography–tandem mass spectrometry. J Chromatogr A 1463:20–31. doi: 10.1016/j.chroma.2016.08.008

Patel K, Fussell RJ, Hetmanski M, Goodall DM, Keely BJ (2005) Evaluation of gas chromatography–tandem quadrupole mass spectrometry for the determination of organochlorine pesticides in fats and oils. J Chromatogr A 1068:289–296. doi: 10.1016/j.chroma.2005.01.040

Pedersen-Bjergaard S, Rasmussen KE (1999) Liquid−liquid−liquid microextraction for sample preparation of biological fluids prior to capillary electrophoresis. Anal Chem 71:2650–2656. doi: 10.1021/ac990055n

Peng X, Pang J, Deng A (2011) Determination of seven phenoxyacid herbicides in environmental water by high performance liquid chromatography coupled with three phase hollow fiber liquid phase microextraction. Se Pu 29:1199–204. PMID: 22500447

Pinto MI, Micaelo C, Vale C, Sontag G, Noronha JP (2014) Screening of priority pesticides in *Ulva* sp. seaweeds by selective pressurized solvent extraction before gas chromatography with electron capture detector analysis. Arch Environ Contam Toxicol 67:547–556. doi: 10.1007/s00244-014-0038-2. doi: 10.1007/s00244-014-0038-2

Poole CF (2003) New trends in solid-phase extraction. TrAC Trends Anal Chem 22:362–373. doi: 10.1016/S0165-9936(03)00605-8

Pose-Juan E, Cancho-Grande B, Rial-Otero R, Simal-Gándara J (2006) The dissipation rates of cyprodinil, fludioxonil, procymidone and vinclozoline during storage of grape juice. Food Control 17:1012–1017. doi: 10.1016/j.foodcont.2005.07.009

Rashidi Nodeh H, Wan Ibrahim WA, Kamboh MA, Sanagi MM (2017) New magnetic graphene-based inorganic–organic sol-gel hybrid nanocomposite for simultaneous analysis of polar and non-polar organophosphorus pesticides from water samples using solid-phase extraction. Chemosphere 166:21–30. doi: 10.1016/j.chemosphere.2016.09.054

Rastrelli L, Totaro K, De Simone F (2002) Determination of organophosphorus pesticide residues in Cilento (Campania, Italy) virgin olive oil by capillary gas chromatography. Food Chem 79:303–305. doi: 10.1016/S0308-8146(02)00143-7

Ravelo-Pérez LM, Hernández-Borges J, Borges-Miquel TM, Rodríguez-Delgado MA (2008a) Pesticide analysis in tomatoes by solid-phase microextraction and micellar electrokinetic chromatography. J Chromatogr A 1185:151–154. doi: 10.1016/j.chroma.2008.01.069

Ravelo-Pérez LM, Hernández-Borges J, Rodríguez-Delgado MÁ (2008b) Multi-walled carbon nanotubes as efficient solid-phase extraction materials of organophosphorus pesticides from apple, grape, orange and pineapple fruit juices. J Chromatogr A 1211:33–42. doi: 10.1016/j.chroma.2008.09.084

Regueiro J, Llompart M, Garcia-Jares C, Garcia-Monteagudo JC, Cela R (2008) Ultrasound-assisted emulsification–microextraction of emergent contaminants and pesticides in environmental waters. J Chromatogr A 1190:27–38. doi: 10.1016/j.chroma.2008.02.091

Ren D, Sun C, Ma G, Yang D, Zhou C, Xie J, Li Y (2018) Determination of pyrethroids in tea brew by GC-MS combined with SPME with multiwalled carbon nanotube coated fiber. Int J Anal Chem 2018:8426598. doi: 10.1155/2018/8426598

Ren ZF, Huang ZP, Xu JW, Wang JH, Bush P, Siegal MP, Provencio PN (1998) Synthesis of large arrays of well-aligned carbon nanotubes on glass. Science 282:1105–1107. doi: 10.1126/science.282.5391.1105

Rezaee M, Assadi Y, Milani Hosseini M-R, Aghaee E, Ahmadi F, Berijani S (2006) Determination of organic compounds in water using dispersive liquid–liquid microextraction. J Chromatogr A 1116:1–9. doi: 10.1016/j.chroma.2006.03.007

Rezić I, Horvat AJM, Babić S, Kaštelan-Macan M (2005) Determination of pesticides in honey by ultrasonic solvent extraction and thin-layer chromatography. Ultrason Sonochem 12:477–481. doi: 10.1016/j.ultsonch.2004.07.004

Rissato SR, Galhiane MS, Apon BM, Arruda MSP (2005) Multiresidue analysis of pesticides in soil by supercritical fluid extraction/gas chromatography with electron-capture detection and confirmation by gas chromatography-mass spectrometry. J Agric Food Chem 53:62–69. doi: 10.1021/jf048772s

Rissato SR, Galhiane MS, Knoll FRN, Apon BM (2004) Supercritical fluid extraction for pesticide multiresidue analysis in honey: determination by gas chromatography with electron-capture and mass spectrometry detection. J Chromatogr A 1048:153–159. doi: 10.1016/j.chroma.2004.07.053

Rodrigues SA, Caldas SS, Primel EG (2010) A simple; efficient and environmentally friendly method for the extraction of pesticides from onion by matrix solid-phase dispersion with liquid chromatography–tandem mass spectrometric detection. Anal Chim Acta 678:82–89. doi: 10.1016/j.aca.2010.08.026

Romero-González R, Pastor-Montoro E, Martínez-Vidal JL, Garrido-Frenich A (2006) Application of hollow fiber supported liquid membrane extraction to the simultaneous determination of pesticide residues in vegetables by liquid chromatography/mass spectrometry. Rapid Commun Mass Spectrom 20:2701–2708. doi: 10.1002/rcm.2653

Rutkowska E, Łozowicka B, Kaczyński P (2018) Modification of multiresidue QuEChERS protocol to minimize matrix effect and improve recoveries for determination of pesticide residues in dried herbs followed by GC-MS/MS. Food Anal Methods 11:709–724. doi: 10.1007/s12161-017-1047-3

Salemi A, Rasoolzadeh R, Nejad MM, Vosough M (2013) Ultrasonic assisted headspace single drop micro-extraction and gas chromatography with nitrogen-phosphorus detector for determination of organophosphorus pesticides in soil. Anal Chim Acta 769:121–126. doi: 10.1016/j.aca.2013.01.054

Samsidar A, Siddiquee S, Shaarani SM (2018) A review of extraction, analytical and advanced methods for determination of pesticides in environment and foodstuffs. Trends Food Sci Technol 71:188–201. doi: 10.1016/j.tifs.2017.11.011

San Román I, Alonso ML, Bartolomé L, Alonso RM (2012) Hollow fibre-based liquid-phase microextraction technique combined with gas chromatography–mass spectrometry for the determination of pyrethroid insecticides in water samples. Talanta 100:246–253. doi: 10.1016/j.talanta.2012.04.039

Sanagi MM, Abbas HH, Ibrahim WAW, Aboul-Enien HY (2012) Dispersive liquid-liquid microextraction method based on solidification of floating organic droplet for the determination of triazine herbicides in water and sugarcane samples. Food Chem 133:557–562. doi: 10.1016/j.foodchem.2012.01.036

Sanchez Costa L, Rodríguez Martínez P, Medina Sala M (2018) Determination of 23 organochlorine pesticides in animal feeds by GC-MS/MS after QuEChERS with EMR-lipid clean-up. Anal Methods 10:5171–5180. doi: 10.1039/c8ay01436a

Sánchez R, Cortes JM, Vazquez A, Villén-Altamirano J, Villén J (2006) Analysis of pesticide residues by online reversed-phase liquid chromatography-gas chromatography in the oil from olives grown in an experimental plot. Part II. J Sci Food Agric 86:1926–1931. doi: 10.1002/jsfa.2565

Sandra P, Tienpont B, David F (2003) Multi-residue screening of pesticides in vegetables, fruits and baby food by stir bar sorptive extraction–thermal desorption–capillary gas chromatography–mass spectrometry. J Chromatogr A 1000:299–309. doi: 10.1016/S0021-9673(03)00508-9

Sandra P, Tienpont B, Vercammen J, Tredoux A, Sandra T, David F (2001) Stir bar sorptive extraction applied to the determination of dicarboximide fungicides in wine. J Chromatogr A 928:117–126. doi: 10.1016/S0021-9673(01)01113-X

Santana-Mayor Á, Socas-Rodríguez B, Herrera-Herrera A V., Rodríguez-Delgado MÁ (2019) Current trends in QuEChERS method. A versatile procedure for food, environmental and biological analysis. TrAC Trends Anal Chem 116:214–235. doi: 10.1016/j.trac.2019.04.018

Sarafraz-Yazdi A, Amiri A (2010) Liquid-phase microextraction. TrAC Trends Anal Chem 29:1–14. doi: 10.1016/j.trac.2009.10.003

Sartori RB, Higino ML, Bastos LHP, Mendes MF (2017) Supercritical extraction of pesticides from banana:

Experimental and modeling. J Supercrit Fluids 128:149–158. doi: 10.1016/j.supflu.2017.05.027

Shen G, Lee HK (2002) Hollow fiber-protected liquid-phase microextraction of triazine herbicides. Anal Chem 74:648–654. doi: 10.1021/ac010561o

Snyder JL, Grob RL, McNally ME, Oostdyk TS (1993) The effect of instrumental parameters and soil matrix on the recovery of organochlorine and organophosphate pesticides from soils using supercritical fluid extraction. J Chromatogr Sci 31:183–191. doi: 10.1093/chromsci/31.5.183

Song W, Zhang Y, Li G, Chen H, Wang H, Zhao Q, He D, Zhao C, Ding L (2014) A fast, simple and green method for the extraction of carbamate pesticides from rice by microwave assisted steam extraction coupled with solid phase extraction. Food Chem 143:192–198. doi: 10.1016/j.foodchem.2013.07.101

Souza-Silva ÉA, Gionfriddo E, Pawliszyn J (2015a) A critical review of the state of the art of solid-phase microextraction of complex matrices II. Food analysis. TrAC Trends Anal Chem 71:236–248. doi: 10.1016/j.trac.2015.04.018

Souza-Silva ÉA, Ruifen J, Rodríguez-Lafuente A, Gionfriddo E, Pawliszyn J (2015b) A critical review of the state of the art of solid-phase microextraction of complex matrices I. Environmental analysis. Trends Anal Chem 71:224–235. doi: 10.1016/j.trac.2015.04.016

Souza Silva ÉA, Pawliszyn J (2012) Optimization of fiber coating structure enables direct immersion solid phase microextraction and high-throughput determination of complex samples. Anal Chem 84:6933–6938. doi: 10.1021/ac301305u

Sparr Eskilsson C, Björklund E (2000) Analytical-scale microwave-assisted extraction. J Chromatogr A 902:227–250. doi: 10.1016/S0021-9673(00)00921-3

Stocka J, Tankiewicz M, Biziuk M, Namieśnik J (2011) Green aspects of techniques for the determination of currently used pesticides in environmental samples. Int J Mol Sci 12:7785–7805. doi: 10.3390/ijms12117785

Sun X, Zhu F, Xi J, Lu T, Liu H, Tong Y, Ouyang G (2011) Hollow fiber liquid-phase microextraction as clean-up step for the determination of organophosphorus pesticides residues in fish tissue by gas chromatography coupled with mass spectrometry. Mar Pollut Bull 63:102–107. doi: 10.1016/j.marpolbul.2011.03.038

Tan GH, Vijayaletchumy K (1994) Determination of organochlorine pesticide residues in river sediments by Soxhlet extraction with hexane-acetone. Pestic Sci 40:121–126. doi: 10.1002/ps.2780400206

Tian F, Liu W, Fang H, An M, Duan S (2014) Determination of six organophosphorus pesticides in water by single-drop microextraction coupled with GC-NPD. Chromatographia 77:487–492. doi: 10.1007/s10337-013-2609-1

Tian L, Huang D, Shi Y, Han F, Wang Y, Ye H, Tang Y, Yu H (2019) Method for the analysis of 7 indictor polychlorinated biphenyls (PCBs) and 13 organochlorine pesticide residues in sediment by gas chromatography (GC). IOP Conf Ser Earth Environ Sci 237:022053. doi: 10.1088/1755-1315/237/2/022053

Tuzimski T, Rejczak T (2016) Application of HPLC-DAD after SPE/QuEChERS with ZrO_2-based sorbent in d-SPE clean-up step for pesticide analysis in edible oils. Food Chem 190:71–79. doi: 10.1016/j.foodchem.2015.05.072

Valverde-García A, Fernández-Alba AR, Agüera A, Contreras M (1995) Extraction of methamidophos residues from vegetables with supercritical fluid carbon dioxide. J AOAC Int 78:867–873. PMID: 7756903

Vazquez-Roig P, Picó Y (2015) Pressurized liquid extraction of organic contaminants in environmental and food samples. TrAC Trends Anal Chem 71:55–64. doi: 10.1016/j.trac.2015.04.014

Walorczyk S (2008) Development of a multi-residue method for the determination of pesticides in cereals and dry animal feed using gas chromatography–tandem quadrupole mass spectrometry: II. Improvement and extension to new analytes. J Chromatogr A 1208:202–214. doi: 10.1016/j.chroma.2008.08.068

Wan Ibrahim WA, Nodeh HR, Aboul-Enein HY, Sanagi MM (2015) Magnetic solid-phase extraction based on modified ferum oxides for enrichment, preconcentration, and isolation of pesticides and selected pollutants. Crit Rev Anal Chem 45:270–287. doi: 10.1080/10408347.2014.938148

Wang D, You J, Lydy MJ (2010) Sediment matrix effects in analysis of pyrethroid insecticides using gas chromatography–mass spectrometry. Arch Environ Contam Toxicol 59:382–392. doi: 10.1007/s00244-010-9506-5

Wang H, Li G, Zhang Y, Chen H, Zhao Q, Song W, Xu Y, Jin H, Ding L (2012a) Determination of triazine herbicides in cereals using dynamic microwave-assisted extraction with solidification of floating organic drop followed by high-performance liquid chromatography. J Chromatogr A 1233:36–43. doi: 10.1016/j.chroma.2012.02.034

Wang H, Yan H, Qiao J (2012b) Miniaturized matrix solid-phase dispersion combined with ultrasound-assisted dispersive liquid-liquid microextraction for the determination of three pyrethroids in soil. J Sep Sci 35:292–298. doi: 10.1002/jssc.201100753

Wang Q, Chen R, Shatner W, Cao Y, Bai Y (2019) State-of-the-art on the technique of dispersive liquid-liquid microextraction. Ultrason Sonochem 51:369–377. doi: 10.1016/j.ultsonch.2018.08.010

Wang R, Su P, Zhong Q, Zhang Y, Yang Y (2013) Ionic liquid-based microwave-assisted extraction of organochlorine pesticides from soil. J Liq Chromatogr Relat Technol 36:687–699. doi: 10.1080/10826076.2012.673207

Wang S, Zhao P, Min G, Fang G (2007a) Multi-residue determination of pesticides in water using multi-walled carbon nanotubes solid-phase extraction and gas chromatography–mass spectrometry. J Chromatogr A 1165:166–171. doi: 10.1016/j.chroma.2007.07.061

Wang W, Meng B, Lu X, Liu Y, Tao S (2007b) Extraction of polycyclic aromatic hydrocarbons and organochlorine pesticides from soils: A comparison between Soxhlet extraction, microwave-assisted extraction and accelerated solvent extraction techniques. Anal Chim Acta 602:211–222. doi: 10.1016/j.aca.2007.09.023

Wang Y-L, You L-Q, Mei Y-W, Liu J-P, He L-J (2016) Benzyl functionalized ionic liquid as new extraction solvent of dispersive liquid-liquid microextraction for enrichment of organophosphorus pesticides and aromatic compounds. Chinese J Anal Chem 44:942–949. doi: 10.1016/S1872-2040(16)60937-4

Wang Y, Sun Y, Xu B, Li X, Wang X, Zhang H, Song D (2015) Matrix solid-phase dispersion coupled with magnetic ionic liquid dispersive liquid–liquid microextraction for the determination of triazine herbicides in oilseeds. Anal Chim Acta 888:67–74. doi: 10.1016/j.aca.2015.07.028

Wilkowska A, Biziuk M (2011) Determination of pesticide residues in food matrices using the QuEChERS methodology. Food Chem 125:803–812. doi: 10.1016/j.foodchem.2010.09.094

Williams DBG, George MJ, Marjanovic L (2014) Rapid detection of atrazine and metolachlor in farm soils: gas chromatography–mass spectrometry-based analysis using the bubble-in-drop single drop microextraction enrichment method. J Agric Food Chem 62:7676–7681. doi: 10.1021/jf502411t

Williams DBG, George MJ, Meyer R, Marjanovic L (2011) Bubbles in solvent microextraction: the influence of intentionally introduced bubbles on extraction efficiency. Anal Chem 83:6713–6716. doi: 10.1021/ac201323z

Wu C, Liu H, Liu W, Wu Q, Wang C, Wang Z (2010) Determination of organophosphorus pesticides in environmental water samples by dispersive liquid–liquid microextraction with solidification of floating organic droplet followed by high-performance liquid chromatography. Anal Bioanal Chem 397:2543–2549. doi: 10.1007/s00216-010-3790-9

Wu J, Ee KH, Lee HK (2005) Automated dynamic liquid–liquid–liquid microextraction followed by high-performance liquid chromatography-ultraviolet detection for the determination of phenoxy acid herbicides in environmental waters. J Chromatogr A 1082:121–127. doi: 10.1016/j.chroma.2005.05.077

Wu L, Hu M, Li Z, Song Y, Yu C, Zhang H, Yu A, Ma Q, Wang Z (2016) Dynamic microwave-assisted extraction combined with continuous-flow microextraction for determination of pesticides in vegetables. Food Chem 192:596–602. doi: 10.1016/j.foodchem.2015.07.055

Wu S, Jin T, Cheng J, Zhou H, Cheng M (2015) Air-assisted liquid liquid-microextraction for the analysis of fungicides from environmental water and juice samples. J Chromatogr Sci 53:1007–1012. doi: 10.1093/chromsci/bmu136

Xiao Q, Hu B, Yu C, Xia L, Jiang Z (2006) Optimization of a single-drop microextraction procedure for the determination of organophosphorus pesticides in water and fruit juice with gas chromatography-flame photometric detection. Talanta 69:848–855. doi: 10.1016/j.talanta.2005.11.024

Yang Y, Liu M, Xu S, Hou L, Ou D, Liu H, Cheng S, Hofmann T (2006) HCHs and DDTs in sediment-dwelling animals from the Yangtze Estuary, China. Chemosphere 62:381–389. doi: 10.1016/j.chemosphere.2005.04.102

Ye C-L, Zhou Q-X, Wang X-M (2006) Headspace liquid-phase microextraction using ionic liquid as extractant for the preconcentration of dichlorodiphenyltrichloroethane and its metabolites at trace levels in water samples. Anal Chim Acta 572:165–171. doi: 10.1016/j.aca.2006.05.052

Yiantzi E, Psillakis E, Tyrovola K, Kalogerakis N (2010) Vortex-assisted liquid-liquid microextraction of octylphenol, nonylphenol and bisphenol-A. Talanta 80:2057–2062. doi: 10.1016/j.talanta.2009.11.005

You J, Wang D, Lydy MJ (2010) Determination of pyrethroid insecticides in sediment by gas chromatography—Ion trap tandem mass spectrometry. Talanta 81:136–141. doi: 10.1016/j.talanta.2009.11.050

You X, Xing Z, Liu F, Jiang N (2013) Air-assisted liquid-liquid microextraction used for the rapid determination of organophosphorus pesticides in juice samples. J Chromatogr A 1311:41–47. doi: 10.1016/j.chroma.2013.08.080

Yu H, Ho TD, Anderson JL (2013) Ionic liquid and polymeric ionic liquid coatings in solid-phase microextraction. TrAC Trends Anal Chem 45:219–232. doi: 10.1016/j.trac.2012.10.016

Yu X, Yang H (2017) Pyrethroid residue determination in organic and conventional vegetables using liquid-solid extraction coupled with magnetic solid phase extraction based on polystyrene-coated magnetic nanoparticles. Food Chem 217:303–310. doi: 10.1016/j.foodchem.2016.08.115

Zayats MF, Leschev SM, Petrashkevich NV, Zayats MA, Kadenczki L, Szitás R, Dobrik HS, Keresztény N (2013) Distribution of pesticides in *n*-hexane/water and *n*-hexane/acetonitrile systems and estimation of possibilities of their extraction isolation and preconcentration from various matrices. Anal Chim Acta 774:33–43. doi: 10.1016/j.aca.2013.03.003

Zhang J, Lee HK (2010) Headspace ionic liquid-based microdrop liquid-phase microextraction followed by microdrop thermal desorption-gas chromatographic analysis. Talanta 81:537–542. doi: 10.1016/j.talanta.2009.12.039

Zhang J, Lee HK (2006) Application of liquid-phase microextraction and on-column derivatization combined with gas chromatography–mass spectrometry to the determination of carbamate pesticides. J Chromatogr A 1117:31–37. doi: 10.1016/j.chroma.2006.03.102

Zhang L, Gionfriddo E, Acquaro V, Pawliszyn J (2018) Direct immersion solid-phase microextraction analysis of multi-class contaminants in edible seaweeds by gas chromatography-mass spectrometry. Anal Chim Acta 1031:83–97. doi: 10.1016/j.aca.2018.05.066

Zhang S, Li C, Song S, Feng T, Wang C, Wang Z (2010) Application of dispersive liquid-liquid microextraction combined with sweeping micellar electrokinetic chromatography for trace analysis of six carbamate pesticides in apples. Anal Methods 2:54–62. doi: 10.1039/b9ay00115h

Zhang S, Yang X, Yin X, Wang C, Wang Z (2012a) Dispersive liquid-liquid microextraction combined with sweeping micellar electrokinetic chromatography for the determination of some neonicotinoid insecticides in cucumber samples. Food Chem 133:544–550. doi: 10.1016/j.foodchem.2012.01.028

Zhang S, Yin X, Yang Q, Wang C, Wang Z (2011) Determination of some sulfonylurea herbicides in soil by a novel liquid-phase microextraction combined with sweeping micellar electrokinetic chromatography. Anal Bioanal Chem 401:1071–1081. doi: 10.1007/s00216-011-5138-5

Zhang Y, Wang X, Lin C, Fang G, Wang S (2012b) A novel SPME fiber chemically linked with 1-vinyl-3-hexadecylimidazolium hexafluorophosphate ionic liquid coupled with GC for the simultaneous determination of pyrethroids in vegetables. Chromatographia 75:789–797. doi: 10.1007/s10337-012-2244-2

Zhang Y, Zhang X, Jiao B (2014) Determination of ten pyrethroids in various fruit juices: Comparison of dispersive liquid-liquid microextraction sample preparation and QuEChERS method combined with dispersive liquid-liquid microextraction. Food Chem 159:367–373. doi: 10.1016/j.foodchem.2014.03.028

Zhao E, Han L, Jiang S, Wang Q, Zhou Z (2006) Application of a single-drop microextraction for the analysis of organophosphorus pesticides in juice. J Chromatogr A 1114:269–273. doi: 10.1016/j.chroma.2006.03.011

Zhao E, Zhao W, Han L, Jiang S, Zhou Z (2007) Application of dispersive liquid–liquid microextraction for the analysis of organophosphorus pesticides in watermelon and cucumber. J Chromatogr A 1175:137–140. doi: 10.1016/j.chroma.2007.10.069

Zhao P, Wang L, Zhou L, Zhang F, Kang S, Pan C (2012) Multi-walled carbon nanotubes as alternative reversed-dispersive solid phase extraction materials in pesticide multi-residue analysis with QuEChERS method. J Chromatogr A 1225:17–25. doi: 10.1016/j.chroma.2011.12.070

Zhao R-S, Diao C-P, Wang X, Jiang T, Yuan J-P (2008) Rapid determination of amide herbicides in environmental water samples with dispersive liquid–liquid microextraction prior to gas chromatography–mass spectrometry. Anal Bioanal Chem 391:2915–2921. doi: 10.1007/s00216-008-2208-4

Zheng G, Han C, Liu Y, Wang J, Zhu M, Wang C, Shen Y (2014) Multiresidue analysis of 30 organochlorine pesticides in milk and milk powder by gel permeation chromatography-solid phase extraction-gas chromatography-tandem mass spectrometry. J Dairy Sci 97:6016–6026. doi: 10.3168/jds.2014-8192

Zhou Q, Wang W, Xiao J (2006) Preconcentration and determination of nicosulfuron, thifensulfuron-methyl and metsulfuron-methyl in water samples using carbon nanotubes packed cartridge in combination with high performance liquid chromatography. Anal Chim Acta 559:200–206. doi: 10.1016/j.aca.2005.11.079

Zougagh M, Valcárcel M, Ríos A (2004) Supercritical fluid extraction: A critical review of its analytical usefulness. TrAC Trends Anal Chem 23:399–405. doi: 10.1016/S0165-9936(04)00524-2

Zuin VG, Schellin M, Montero L, Yariwake JH, Augusto F, Popp P (2006) Comparison of stir bar sorptive extraction and membrane-assisted solvent extraction as enrichment techniques for the determination of pesticide and benzo[a]pyrene residues in Brazilian sugarcane juice. J Chromatogr A 1114:180–187. doi: 10.1016/j.chroma.2006.03.035

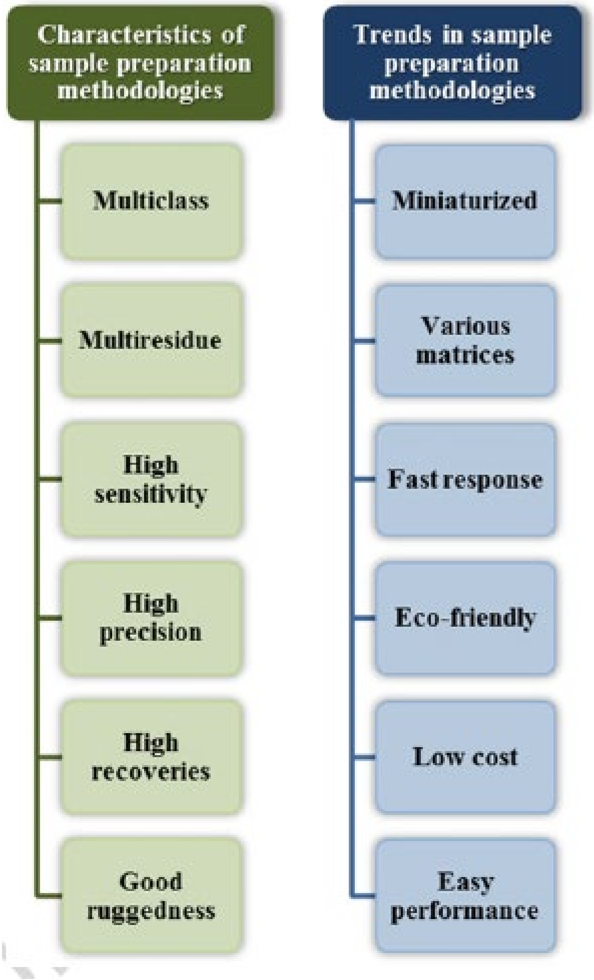

Figure 1. Analytical characteristics and trends for sample preparation methods in pesticide residue analysis.

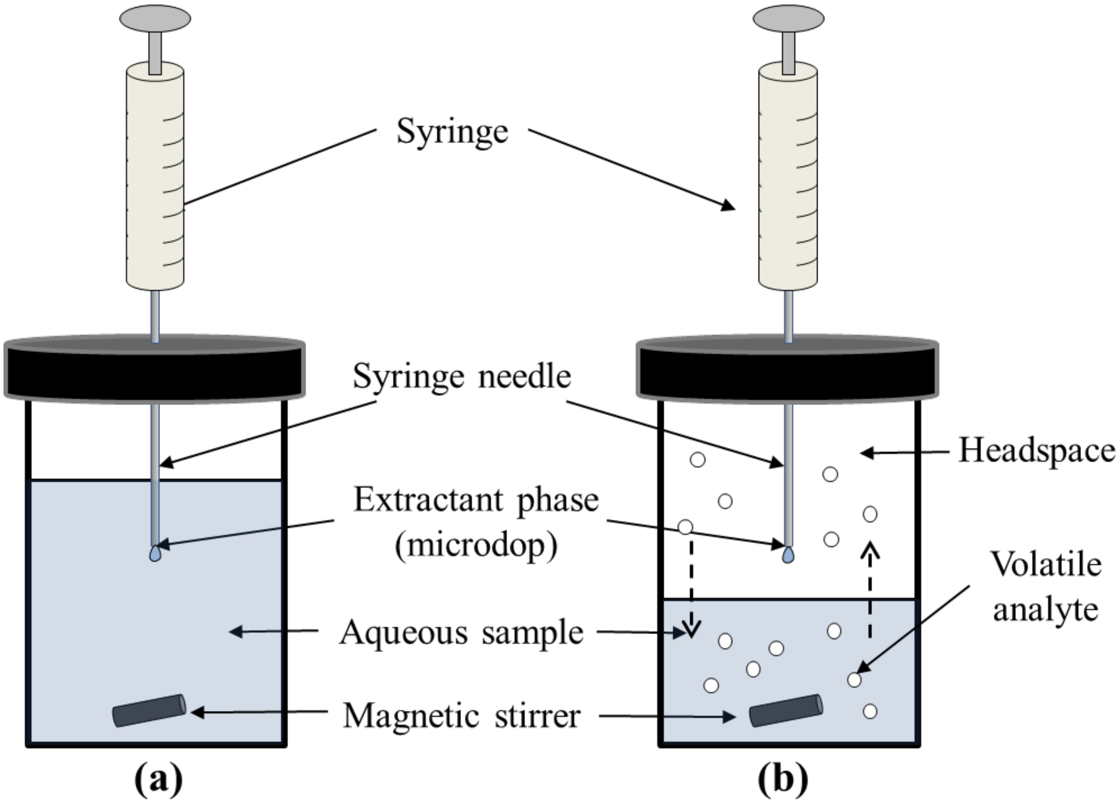

Figure 2. Principle of single-drop microextraction: (a) Direct immersion; (b) Headspace.

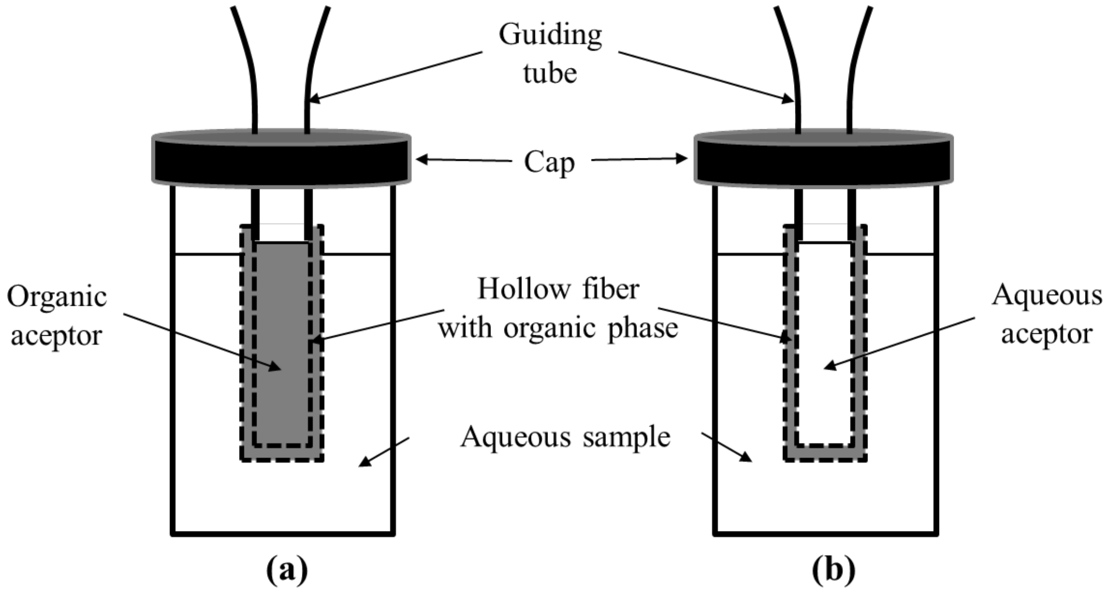

Figure 3. Principle of hollow-fiber liquid-phase microextraction: (a) two-phase; (b) three phase (modified after Han and Row 2012).

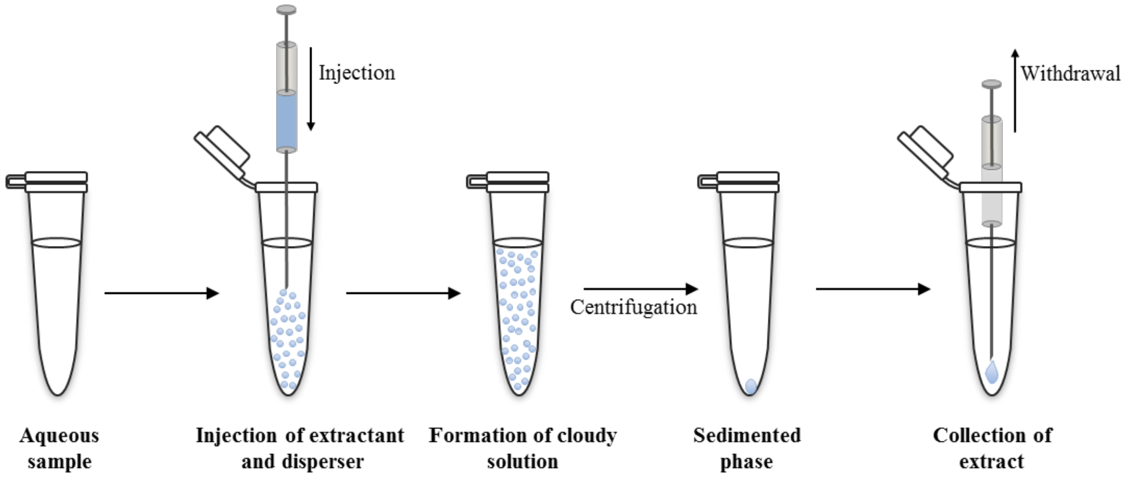

Figure 4. Principle of dispersive liquid-liquid microextraction.

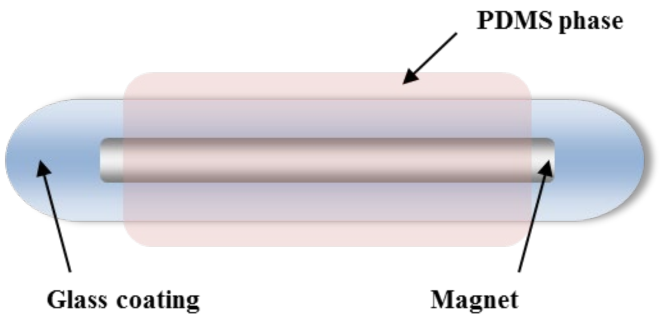

Figure 5. Stir bar sorptive extraction device (PDMS: polydimethylsiloxane)