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Analytical Methods

Applications of sample preparation techniques in the analysis of pesticides and PCBs in food

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Abstract

Pesticides and polychlorinated biphenyls (PCBs) are found in various parts of the environment in quite small concentrations, but they accumulate and thus become a threat to human health and life. A review is focused on the application of some popular techniques for sample preparation in analysis of these compounds in food. Even with the emergence of advanced techniques of final analysis, complex matrices, such as food, require extensive sample extraction and purification. Traditional sample preparation techniques are time consuming and require large amount of solvents, which are expensive, generate considerable waste, contaminate the sample and can enrich it for analytes. There have been many sample preparation techniques proposed to meet the requirements connected with the multiplicity of food. Optimal sample preparation can reduce analysis time, sources of error, enhance sensitivity and enable unequivocal identification and quantification. Sample extraction and purification techniques are discussed and their most recent applications in food analysis are provided. This review pointed out that sample preparation is the critical step.

Keywords: Pesticides; Polychlorinated biphenyls; Review; Food; Sample preparation; Extraction; Purification

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Abbreviations: ASE, accelerated solvent extraction; FMASE, focused microwave-assisted Soxhlet extraction; GC, gas chromatography; GPC, gel permeation chromatography; HCDS, high capacity disposable silica columns; HPLC, high performance liquid chromatography; LC, liquid chromatography; LE, liquid extraction; LLE, liquid–liquid extraction; MAE, microwave-assisted extraction; MASE, membrane-assisted solvent extraction; MMLLE, microporous membrane liquid–liquid extraction; MSPD, matrix solid phase dispersion; PCBs, polychlorinated biphenyls; PFE, pressurized fluid extraction; PME, polymeric membrane extraction; SBSE, stir-bar sorptive extraction; SFE, supercritical fluid extracition; SPE, solid phase extraction; SPME, solid phase microextraction.

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1. Introduction

Pesticides and polychlorinated biphenyls (PCBs) have been widely used throughout the world since the middle of the last century; however, most of them have been banned since the 1970s (many of the organochlorine compounds). Pesticides were mainly used in agriculture and animal production and PCBs as industrial fluids, both including substances with high toxic effects and persistence in the environment, posing considerable hazards. The problem becomes more serious when bioaccumulation of these lipophilic compounds is taken into consideration (Biziuk, 2001; Doyle, 2004).

Due to the general prevalence of pesticides and PCBs, it is important to investigate the concentration levels of PCB, pesticides and their metabolites in environmental samples, especially in food (Lebel et al., 1998).

For these reasons, reliable analytical methods are required and analytical chemists have to contend with a variety of diluted contaminations, including not only parent substances but also their metabolites. Due to the low detection levels required by regulatory bodies and the complex nature of the matrices in which the target compounds are present, efficient sample preparation and trace-level detection and identification are important aspects of analytical methods (Ahmed, 2001; Albero, Brunete, & Tadeo, 2005; Liu, Hashi, Qin, Zhou, & Lin, 2007; Soler & Pico, 2007; Torres, Pico, & Manes, 1996; Zambonin, Quinto, Vietro, & Palmisano, 2004). After sampling, it is necessary to prepare the sample for the determination of analytes through extraction, trace enrichment and interferents' removal (Fig. 1). These procedures often take up most of the total analysis time, contributing highly to the total cost of analysis, and greatly influencing the reliability and accuracy of the analysis (Ahmed, 2001; Namieśnik & Górecki, 2001).

In food analysis, traditional methods for sample preparation are laborious, time consuming and usually involve large amounts of solvents, which are expensive, generate considerable waste, contaminate the sample and can enrich it for analytes. In addition, usually more than one clean-up stage prior to detection is required. As a result, modern sample preparation procedures have been developed or improved to overcome the drawbacks of the traditional approaches. Growing concern over food safety necessitates more rapid and automated procedures to take into account the constant increase in the number of samples to be tested, so interest in procedures that are fast, accurate, precise, solventless, inexpensive and amenable to automation for on-line treatment is ongoing (Buldini, Ricci, & Sharma, 2002; Peris, 2002; Ridgway, Lalljie, & Smith, 2007).

Today special attention is paid to such analytical sample preparation procedures which ensure reduction of the amount of liquid solvents used or their complete elimination in the course of the analytical procedure. A great increase in interest in the so-called solventless method is the result of both ecotoxicology (dumping residual solvents, usually highly toxic, into the environment) and economics (high purity solvents are expensive) (Curyło, Wardencki, & Namieśnik, 2007; Namieśnik, 2001).

This review describes some of the most popular sample preparation procedures to determine pesticides and PCBs in food. Coverage is intended to be comprehensive and also to outline those developments which are in particular relevance to food analysis, especially when using chromatographic techniques. Readers seeking a more detailed discussion are referred to the cited texts.

2. Extraction techniques

An important step in the preparation of food samples prior to final analysis is isolation and/or enrichment. The procedures consist of the transfer of analytes from the primary matrix into the secondary one with a concurrent purging of interfering substances (isolation) and increasing the analytes' concentrations to a level above the detection limit for a given analytical technique (enrichment).

In the case of organic contaminants, such as pesticides and PCBs, in solid phase samples that are typical in food quality analysis, it is necessary to replace the solid matrix

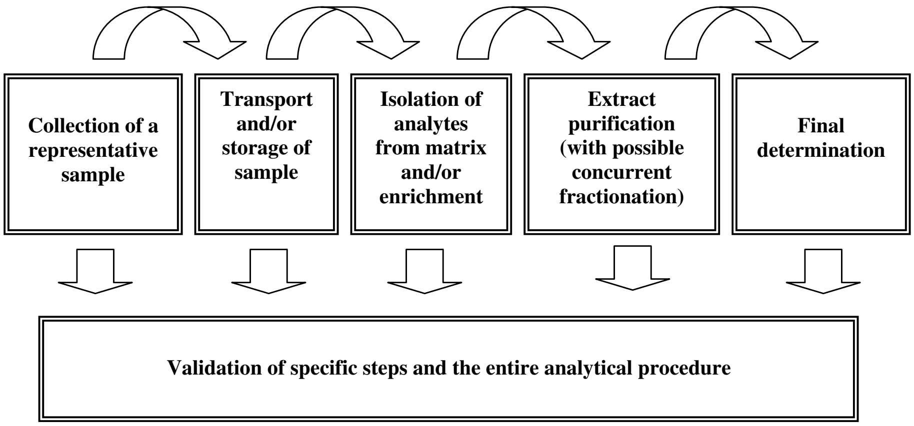

Fig. 1. Main steps of analytical procedures used for determining pesticides and PCBs in food samples.

with a liquid one. For this purpose, an appropriate extraction method should be used. Among the many techniques that exist for isolating pesticides and PCBs from food samples, the most frequently used are:

- solvent extraction by shaking (LE),
- solvent extraction in a Soxhlet or Soxtec apparatus,
- focused microwave-assisted solvent extraction in a Soxhlet apparatus (FMASE),
- ultrasonication extraction (USE),
- microwave-accelerated extraction (MAE),
- accelerated solvent extraction (ASE; also known as PFE or PLE),
- supercritical fluid extraction (SFE),
- membrane extraction techniques,
- solid-based extraction techniques.

Conventional extraction of organic analytes from food samples usually begins with a homogenization step, followed by tedious liquid extraction with one or several clean-up steps, and purification of the extract to remove co-extractants before the sample is subject to final determination (Carabias-Martinez, Rodriguez-Gonzalo, Paniagua-Marcos, & Hernandez-Mendez, 2000). Solvent extraction aided by shaking is based on the partitioning of analytes between liquid and solid phases (in the case of classical liquid-liquid extraction (LLE), between two immiscible liquids), which occurs when analytes move from the sample matrix into the properly selected solvent. When considering this technique, there are many inherent disadvantages, e.g., it is laborious and time-consuming, expensive and apt to form emulsion, it requires the evaporation of large volumes of solvents and the disposal of toxic and flammable chemicals. Moreover, a relatively large amount of matrix is required. Smaller sample sizes become important when dealing with real life problems, such as consumer complaints and alleged chemical contamination. Recent regulations pertaining to the use of organic solvents have made LE unacceptable because of very large amounts of solvents used in this technique.

For these reasons (to reduce the usage of solvents), many innovations can be found in analytical processes that can be applied to food preparation for extraction. This has resulted in the recognition that LE can now be replaced with faster and less expensive techniques. One of these techniques is extraction in a Soxhlet apparatus. Extraction in this equipment is a very common separation technique in food analysis because no filtration is necessary, the extraction temperature is higher than room temperature and the sample is repeatedly brought into contact with fresh solvent. The disadvantages of this technique are that it still requires large amounts of solvent, the solvent must be evaporated to concentrate analytes before determination and the process consist of a single sample run that takes many hours to complete.

An improved version of the Soxhlet apparatus, which allows for shortening of the extraction time even to one hour, with a simultaneous reduction of solvent usage, is Soxtec. Extraction in this apparatus is a two-step procedure, involving a boiling and a rinsing step, which drastically reduces the total time of extraction. It has been used in several applications to extract organochlorine contaminants from samples with high lipid content, e.g., fish (Falandysz et al., 2004).

The use of focused microwave-assisted Soxhlet extraction (FMASE) has proved to be an interesting alternative to Soxhlet extraction. The key aspect of FMASE is that it maintains the advantages of conventional Soxhlet extraction and overcomes the shortcomings of conventional Soxhlet by accelerating the process and minimizing environmental pollution due to the small amount of solvent released into the atmosphere (Luque-Garcia & Luque de Castro, 2004). The first fully automated microwave-assisted Soxhlet extractor has been employed for analysing food samples, mainly with regard to fat content; however, it has also been used for determining pesticide residues in sunflower seeds (Garcia-Ayuso, Sanchez, Fernandez de Alba, & Luque de Castro, 1998; Prados-Rosales, Luque Garcia, & Luque de Castro, 2003).

A common conventional technique is ultrasonication extraction (USE), which has been widely applied for the extraction of pesticides and PCBs from various environmental samples (Ahmed, 2003). The main reason for applying acoustic energy is that it enhances food washing. The predominant mechanism for this washing is mechanical, and includes the abrasion of suspended food particles in solvent, leading to the surface removal of contaminants, and improved solvent leaching of contaminants from the interior of the particles (Mason, Collings, & Sumel, 2004). This technique still requires (like other techniques discussed in this section) the application of a solvent.

Some of the applications of the described techniques are presented in Table 1.

Unfortunately, these techniques demand long extraction times and large volumes of highly purified and hazardous organic solvents, generating dirty extracts that involve extensive clean-up before analysis. The main key to shorter extraction times and reduced solvent consumption with techniques including microwave-assisted extraction (MAE), accelerated solvent extraction (ASE) and supercritical fluid extraction (SFE) is the possibility of working at elevated temperatures above the boiling point of the solvent. Thereby the extraction process is facilitated due to increased analyte desorption and diffusion from the solid matrix. Several applications utilizing MAE, ASE and SFE for the extraction of pesticides and PCBs from food have been published and some of them are presented in Table 2.

In the case of microwave-assisted extraction, the phenomenon of microwave energy absorption by the molecules of chemical compounds has been applied. This technique has proven to be better than Soxhlet extraction by cutting solvent consumption and extraction time (Diagne, Foster, & Khan, 2002). MAE utilizes microwave

Table 1
LLE, USE, FMASE, Soxhlet and Soxtec extraction of pesticides and PCBs from food samples

Food	Analytes	Solvent	Technique	Reference
Honey	Organochlorine pesticide residues (11)	Petroleum ether/ethyl acetate (80:20, v:v)	LLE	Tahboub, Zaater, and Barri (2006)
Honey	Pesticides within the major groups of pesticides (48)	Acetonitrile, acetone, ethyl acetate or dichloromethane	LLE	Rissato, Galhiane, Almeida, Gerenutti, and Apon (2007)
Butter	PCBs	Hexane, and acetone/hexane (2:1, v:v)	LLE	Ramos, Eljarrat, Hernandez, Rivera, and Gonzalez (1999)
Fruits and vegetables	Pesticides and their metabolites (57)	Ethyl acetate	LLE	Jansson, Pihlstrom, Osterdah, and Markides (2004)
Olive oil	Organophosphorus insecticides	Acetonitrile, acetonitrile/acetone (3:1, v:v), acetonitrile/hexane (3:1, v:v)	USE	Lentza-Rizos, Avramides, and Cherasco (2001)
Pepper, broccoli, tomato, orange, lemon, apple and melon	Selected multi-class pesticides	Methanol	USE	Ferrer, Garcia-Reyes, Mezcua, Thurman, and Fernandez-Alba (2005)
Chicken liver	Chlorinated pesticides	Hexane/acetone (4:1, v:v)	USE	Lambropoulou et al. (2006)
Beans	Fenitrothion	Dichloromethane	Soxhlet extraction	Diagne et al. (2002)
Milk	PCBs	Pentane/dichloromethane (1:1, v:v)	Soxhlet extraction	Focant et al. (2002)
Poultry, pork and lamb	Organochlorine and organophosphorus pesticides	Ethyl acetate	Soxhlet extraction	Garrido Frenich et al. (2006)
Fish	Organochlorine pesticides	Hexane/acetone (1:1, v:v)	Soxhlet extraction	Fidalgo-Used, Centineo, Blanco-Gonzalez, and Sanz-Medel (2003)
Fish	PCBs	Hexane	Soxtec extraction	Falandysz et al. (2004)
Sunflower seeds	Pesticide residues	Dichloromethane	FMASE	Prados-Rosales et al. (2003)

energy to cause molecular movement and liquid rotation with permanent dipole, leading to very fast heating of the solvent and the sample. The main advantages of microwave pretreatment are the low temperature requirement, high extraction rate, automation and the possibility of simultaneously extracting different samples at the same time without interferences (Camel, 2000).

One of the latest contributions to the increasing number of extraction techniques is accelerated solvent extraction. This technique utilizes solvents that are raised to the near-supercritical region, where they show better extraction properties. At high temperatures, the rate of extraction increases because the viscosity and the surface tension decreases, while its solubility and diffusion rate into the sample increase. Pressure keeps the solvent below its boiling point and forces its penetration into the pores of the sample. The combined use of high pressures and temperatures provides a faster extraction process that requires smaller amounts of solvent compared with traditional extraction, thus decreasing the dilution of the sample (Mendiola, Herrero, Cifuentes, & Ibanez, 2007). The time required for extraction is practically independent of the sample mass and the efficiency of extraction is mainly dependent on temperature. Comparing ASE to LLE or Soxhlet extraction, the advantage of reducing solvent consumption and extraction time contrast with the disadvantage of using very expensive and specialized equipment. However, the major problem with fatty matrices is the presence of large amounts of co-extracted lipids, which means that post-clean-up of the extract is required to carry out lipid elimination. To overcome this drawback, simultaneous extraction-purification methods for pesticides and PCBs in biota samples using ASE have been developed. Alumina (Dionex Application Note 322, 2000), sulphuric acid impregnated silica gel (Muller, Bjorklund, & von Holst, 2001) and *Florisil* (Gomez-Ariza, Bujalance, Giraldez, Velasco, & Morales, 2002), to name a few, were successfully used as a retainer sorbent inside the ASE cell. Automation of this process allows the extraction of a large number of samples, either sequentially (ASE 200, Dionex, Sunnyvale, CA, USA) or in parallel (FAST-PSE, Applied Instrumentation, Allentown, PA, USA). A very detailed description of the main principles on which accelerated solvent extraction is based can be found in numerous review articles in the literature (Bjorklund, Sporring, Wiberg, Haglund & von Holst, 2006; Giergielewicz-Możajska, Dąbrowski, & Namieśnik, 2001; Ramos, Kristenson, & Brinkman, 2002; Schantz, 2006).

Another attractive alternative to traditionally used techniques is supercritical fluid extraction. The solvent used is this technique a supercritical fluid (a substance above its critical temperature and pressure, which diffuses through solids like gases (approximately), but dissolves analytes like liquid). The main advantages of SFE are the possibility of obtaining clean extracts with reduced solvent consumption (zero in many cases) and extraction time, where the extracts can often be analyzed with no further clean-up. In addition, many sample pre-treatments can be done with

Table 2
Applications of MAE, ASE and SFE in food sample preparation

Food	Analytes	Solvent/fluid + modifier/P (bar[a])/T (°C)/t (min) (for SFE)	Technique	Reference
Beans	Fenitrothion	Acetone/hexane (1:1, v:v)	MAE	Diagne et al. (2002)
Fresh and cooked vegetables (cabbage, tomatoes, chillies, potatoes and peppers)	Insecticides thiamethoxam and imidacloprid, fungicide carbendazim	Acetone	MAE	Singh, Foster, and Khan (2004)
Sesame seeds	Organochlorine pesticides (16)	Water/acetonitrile (5:95, v:v)	MAE	Papadakis et al. (2006)
Mussels	Polychlorinated biphenyls	Acetone/hexane (1:1, v:v) or KOH in methanol	MAE	(Xiong, He, and Zhang (2000)
Oranges	Atrazine, organophosphorus pesticides	Acetone/hexane (1:1, v:v)	MAE	Bouaid, Martin-Esteban, Fernandez, and Camara (2000)
Baby food	Malathion, chlorpyrifos, 4,4′-DDE, 4,4′-DDT	Acetonitrile or ethyl acetate	ASE	Chuang et al. (2001)
Oranges and peaches	Benzimidazoles and azoles, organophosphorus, carbamates, neonicotinoids and acaricides	Ethyl acetate	ASE	Blasco, Font, and Pico (2005)
Cod-liver oil, milk powder and feeds	PCBs	Hexane	ASE	Muller et al. (2001)
Cod-liver oil, pork fat and feeds	PCBs	Pentane, hexane or heptane	ASE	Sporring and Bjorklund (2004)
Pork and chicken meat, common two banded sea bream and eggs	PCBs	Hexane	ASE	Ramos, Dietz, Gonzalez, and Ramos (2007)
Fresh vegetables	A wide range of pesticides	Ethyl acetate/acetone (3:1, v:v)	ASE	Garrido Frenich, Martinez Salvador, Martinez Vidal, and Lopez-Lopez (2005)
Fresh pear, cantaloupe, white potato, and cabbage	A wide range of pesticides (28 from 8 pesticide classes)	Acetone/dichloromethane (3:1, v:v)	ASE	Adou, Bontoyan, and Sweeney (2001)
Wheat and maize	Organophosphorus pesticides	CO_2/245/70/5 + 35	SFE	Norman and Panton (2001)
Gazpacho (a table-ready food composite containing crude vegetables, white bread, vegetable oil, water, and other minor components)	Organohalogen and organophosphate pesticides (17)	CO_2 and CO_2 + methanol/300–500/50–90/20	SFE	Aguilera, Brotons, Rodriguez, and Valverde (2003)
Honey	Different pesticides (organochlorine, organophosphorus, organonitrogen and pyrethroid)	CO_2 + acetone/acetonitrile/200–600/40–90/20	SFE	Rissato, Galhiane, Knoll, and Apon (2004)
Spinach, soybean, orange	Different pesticides	CO_2/172/40/15	SFE	Ono, Yamagami, Nishina, and Tobino (2006)
Apple, green bean and carrot	Different pesticides	CO_2/320/60/10–30	SFE	Lehotay (2002)
Cereals, cereal products, vegetables and fruits	Different pesticides (organochlorine, organophosphorus, organonitrogen and pyrethroid)	CO_2/123/50/30 CO_2/202/80/30	SFE	Poustka, Holadova, and Hajsova (2003)
Fish muscle	Organohalogenated pesticides	CO_2/100–240/36–64	SFE	Antunes, Gil, Gabriela, and Gil (2003)

[a] Most commonly employed pressure units in SFE.

nonpolluting, nontoxic supercritical fluids, such as carbon dioxide, which is the most widely used extracting solvent. The technique can also be applied to thermally unstable analytes when selecting supercritical fluids with low critical temperature. Consequently, its role in separation science is pointed out by many reviews (Camel, 1998; Reverchon & De Marco, 2006; Smith, 1999), and some of them concern the use of SFE in food analysis (Brunner, 2005; Mendiola et al., 2007).

The selective nature of membranes has made them a unique alternative to solvent extraction for sample clean up, especially if coupled with chromatographic techniques (Cordero et al., 2000; Jonsson & Mathiasson, 2000). The application of membrane extraction allows the preparation of samples that have a complex matrix by means of simple and easily automated equipment (Jakubowska, Polkowska, & Namieśnik, 2005). Additionally, this technique can be coupled with the chromatographic system with significant advantages – direct introduction of untreated samples, analyte preconcentration, and elimination of interferences, changes in the matrix or the solvent, preservation of the chromatographic system. There is also the possibility of recirculating the sample through the membrane cell, thus allowing the extraction procedure to be applied, even in cases where only very small sample volumes are available (Carabias-Martinez et al., 2000). For this reason, membrane-based extraction methods have been employed in food analysis (Table 3).

Another way of extracting analytes is using a solid adsorbent material. A sorbent with strong affinity towards some target analytes will retain and concentrate those compounds from the sample solution. Widely applied to many matrices, including food, solid-phase-based extraction techniques are matrix solid-phase dispersion (MSPD), solid-phase extraction (SPE), solid-phase microextraction (SPME) and stir-bar sorptive extraction (SBSE). Current trends in these techniques for pesticide determination in food and the environment are presented in an up-to-date review (Pico, Fernandez, Ruiz, & Font, 2007). Some recent applications of these techniques are presented in Table 4.

Solid-phase extraction involves the use of disposable cartridges and disks to trap analytes. As the sample solution passes through the activated sorbent bed, analytes concentrate on its surface, while the other sample components pass through the bed (or vice versa, if necessary for clean-up) (Żwir-Ferenc & Biziuk, 2006). There are many types of sorbent that are commercially available and applied for food analysis, such as alumina, magnesium silicate and graphitised carbon, but the most common material is silica because it is reactive enough to permit its surface to be modified by chemical reactions and yet stable enough to allow its use with a wide range of solutions. This technique offers many improvements over LLE and permits simultaneous removal of interfering substances and concentrations of analytes. Using SPE, multiple samples can be treated in parallel using relatively small quantities of solvent. When considering the application of this technique to solid matrices (vegetables and fruits), a separate homogenization step, and often, filtration, sonication, centrifugation, and liquid-liquid clean-up are required (Escuderos-Morenas, Santos-Delgado, Rubio-Barroso, & Polo-Diez, 2003; Martel & Zeggane, 2002; Muccio et al., 2006). Another drawback of this technique is that the packing must be uniform to avoid poor efficiency and although pre-packed commercial cartridges are now considered reliable, automated systems can have difficulties with reproducibility for some sample types. The use of highly selective immunosorbents or molecularly imprinted polymers (MIPs) can solve these problems; thifluzamide in peanut samples (Ben Rejeb et al., 2001), imazalil in citrus fruits (Watanabe et al., 2000) and phenylurea herbicides in lemon juice (Pichon, Krasnova, & Hennion, 2004) have so far been rapidly isolated using immunosorbents.

Solid-phase microextraction is a technique that can integrate sampling, extraction, pre-concentration and sample introduction into a single uninterrupted process resulting in high sample throughput (Pico et al., 2007). In SPME, a fiber of silica or other appropriate material, coated with a minute quantity of the extracting phase, where analytes are adsorbed, is exposed to the sample or its headspace. SPE and SPME are different techniques because the former is expected to extract all the target analytes from the sample solution while the latter is a partition process. SPME is very useful for determining analytes from liquid food, in the form of wine (Rial Otero, Yague Ruiz, Cancho Grande, & Simal Gandara, 2002; Wu, Tragas, Lord, & Pawliszyn, 2002) and fruit juice (Sagratini, Manes, Giardina, Damiani, & Pico, 2007). Although the fiber cannot be submerged in a solid, the problem has been resolved by using headspace (HS)-SPME (Dong, Zeng, & Li, 2005; Lambropoulou & Albanis, 2002) or by obtaining an aqueous extract from the sample (Beltran, Peruga, Pitarch, Lopez, & Hernandez, 2003; Berrada, Font, & Molto, 2004), usually avoiding in this way the use of solvents. SPME allows rapid determination of the residues in complex matrices (food) without additional purification steps and couples with GC determination without further handling but the technique suffers from the disadvantage of relatively long equilibration times during the extraction procedure (Wardencki, Michulec, & Curyło, 2004).

A relatively new micro-extraction and pre-concentration technique, which can be easily coupled on-line with LC, is in-tube SPME. This technique uses an open tubular fused-silica as an extraction device. Organic compounds in liquid samples are directly extracted and concentrated into the stationary phase of capillary columns by repeated draw/eject cycles of the sample solution, and they can be directly transferred to the liquid chromatographic column (Kataoka, 2002; Wu et al., 2002). On-line in-tube SPME performed continuous extraction, concentration, desorption, and injection using an autosampler is commonly used in combination with HPLC and LC–MS.

Among these techniques, matrix solid-phase dispersion is an extraction and purification technique used for the

Table 3
Applications of membrane techniques to food sample extraction

Food	Analytes	Technique	Reference
Sugarcane juice	Pesticides	MASE	Zuin et al. (2006)
Red wine, white wine, apple juice	Organophosphorus pesticides (8)	MASE	Schellin, Hauser, and Popp (2004)
Red wine	Pesticides	MMLLE	Hyotylainen, Luthje, Rautiainen-Rama, and Riekkola (2004)
Eggs	Pesticides (10)	PME	Carabias-Martinez et al. (2000)

Table 4
Applications of solid-phase-based extraction techniques for food sample preparation

Food	Analytes	Characteristics	Elution	Technique	Reference
Potatoes	Monolinuron, linuron and chlorbromuron residues	C_8 cartridges	Acetonitrile	SPE	Escuderos-Morenas et al. (2003)
Apricot, peach, pear, celery and courgette	Neonicotinoid pesticides (4)	Extrelut-NT20 cartridges	Dichloromethane	SPE	Muccio et al. (2006)
Honey	Acaricides	C_{18} cartridges	Acetone	SPE	Martel and Zeggane (2002)
Wine	Pesticide residues	Polymeric cartridges (ODS, LiChrolut EN, Oasis)	Ethyl acetate and acetone	SPE	Jimenez, Bernal, de Nozal, Toribio, and Arias (2001)
Oils and citrus fruit	Pesticides (12)	FL-PR cartridges	Dichloromethane	SPE	Barrek, Paisse, and Grenier-Loustalot (2003)
Honey	Pesticides of different chemical families (16)	100 μm PDMS	Desorption at 280 °C for 5 min	SPME	Campillo, Penalver, Aguinaga, and Hernandez-Cordoba (2006)
Carrots, potatoes and onions	Phenylurea herbicides and their homologous anilines	85 μm PA	Desorption at 300 °C for 5 min	SPME	Berrada et al. (2004)
Strawberry and cherry juices	Organophosphorus insecticides	85 μm PA, 100 μm PDMS, 65 μm CW-DVB, 65 μm PDMS-DVB	Desorption at 240 °C for 2 min	HS-SPME	Lambropoulou and Albanis (2002)
Tomatoes and strawberries	Pyrethroid insecticides (7)	100 μm PDMS, 65 μm PDMS-DVB, 75 μm CAR-PDMS, 65 μm CW-DVB, 85 μm PA	Desorption at 270 °C for 5 min	SPME	Beltran et al. (2003)
Wine	Phenylurea (6) and carbamate (6) pesticides	PPY coated on inner surface of a fused-silica capillary	SPME, coupled automated in-tibe to LC desorption with mobile phase	In-tube SPME	Wu et al. (2002)
White Wine	Fungicides cyprodinil and fludioxonil	70 μm PDMS, 85 μm PA, 65 μm CAR-PDMS, 65 μm CW-DVB, 65 μm PDMS-DVB, 50/30 μm DVB-CAR-PDMS	Desorption at 240 °C for 3 min	SPME	Rial Otero et al. (2002)
Apple juice, apple and tomato	Organophosphorus (8)	Vinyl crown ether polar fibers (85 μm B15C5, 80 μm DB18C6, 84 μm PSO18C6), 85 μm PA, 65 μm PDMS-DVB,	Desorption at 270 °C for 5 min	SPME	Cai, Gong, Chen, and Wu (2006)
Radish	Organochlorine pesticides and their metabolites	Calix [4] arene fiber (60 μm)	Desorption at 270 °C for 2 min	HS-SPME	Dong et al. (2005)
Carrot, grape and multivegetable juices	Herbicides (15)	*Florisil*	Ethyl acetate with assisted sonication	MSPD	Albero, Sanchez-Brunete, Donoso, and Tadeo (2004)
Olive and olive oil	Widely used pesticides (12)	Aminopropyl (Bondesil-NH_2, 40 μm particle size)	Acetonitrile	MSPD	Ferrer, Gomez et al. (2005)
Tomato fruit	Glyphosate and aminomethylphosphonic acid	HNO_3 1 M and NH_2-silica	HNO_3 0.01 M	MSPD	Garcia de Llasera, Gomez-Almaraz, Vera-Avila, and Pena-Alvarez (2005)
Citrus fruit (oranges, tangerines, grape fruits and lemons)	Pesticides	C_{18} bonded silica	Dichloromethane/methanol (80:20, v/v)	MSPD	Soler, Manes, and Pico (2005)
Cucumber, potato	Organophosphorus pesticides	A sol/gel PDMS was used to coated bars consisting of an iron bar inside a glass tube	Desorption at 260 °C for 5 min	SBSE	Liu, Hu, Zhao J., Xu, and Guan (2005)
Fruits and vegetables	Azole (1), insert growth regulation (1), pyrethroid (1), pyrrole (1), triazole (4)	Stir bar: 10 mm in length and coated with a 1-mm PDMS layer	Methanol	SBSE	Juan-Garcia, Pico, and Font (2005)

(*continued on next page*)

Table 4 (*continued*)

Food	Analytes	Characteristics	Elution	Technique	Reference
Grapes	Fungicides (6)	C_{18} columns	Dichloromethane/ methanol (50:50, v/v)	SPE	Juan-Garcia, Manes, Font, and Pico (2004)
		Stir bar: 10 mm in length and coated with a 1-mm PDMS layer	Methanol	SBSE	
Fruits and vegetables (28)	Pesticides (15)	Stir bar: 10 mm in length and coated with a 0,5-mm PDMS layer	Desorption at 280 °C for 3 min	SBSE	Kende, Csizmazia, Rikker, Angyal, and Torkos (2006)

The fiber coating: PA – polyacrylate; PDMS – poly(dimethylsiloxane); CW-DVB – carbowax-divinylbenzene; PDMS-DVB – poly(dimethylsiloxane)-divinylbenzene; CAR-PDMS – Carboxen-poly(dimethylsiloxane); Coating (thickness and functional group) and eluent (or desorption) conditions.

simultaneous determination of various pollutants from semisolid and solid samples. This technique comprises sample homogenization, cellular disruption, fractionation, and purification in a single process (Kristenson, Ramos, & Brinkman, 2006). MSPD involves the dispersion of the sample in a solid sorbent, followed by preliminary purification and the elution of the analytes with a relatively small volume of solvent. The extracts obtained are generally ready for analysis, but, if necessary, they can be easily subjected to direct extract purification (Garcinuno, Ramos, Fernandez-Hernando, & Camara, 2004).

Stir-bar sorptive extraction, a recent technique based on the sorptive interaction of the compounds of interest with a coat of polydimethylsiloxane (PDMS) deposited on a magnetic glass, was introduced by Baltussen et al. (Baltussen, Sandra, David, & Cramers, 1999). The extraction mechanism and advantages are similar to those of SPME, but the enrichment factor, which is determined by the amount of extractive phase, is up to 100 times higher. Therefore, SPME is considered ideally suited for the detection of compounds that present high concentrations whereas SBSE is the method of choice for trace analysis (Bicchi, Cordero, Rubiolo, & Sandra, 2003). In this technique, analytes are adsorbed on a magnetic rod, coated with PDMS, by stirring with it for a given time. After that, the stir bar is either thermally desorbed on-line with capillary GC-MS or by organic solvents to be subsequently injected into a chromatographic system (Baltussen, Cramers, & Sandra, 2002; Pico et al., 2007).

3. Extract purification

The isolation (extraction) of the analytes from biological and environmental samples is connected with a specific purification effect, and vice versa, almost each purification process secures a certain degree of analyte isolation (acid digestion and saponification are exceptions). Therefore, it is not possible to precisely define a given isolation and/or purification technique exclusively, as such (Tekel, Hudecova, & Pecnikova, 2001).

During the extraction of food samples, not only the analytes are isolated. There are different types of interfering compounds, mainly fats, carbohydrates, water, chlorophyll and others, which get co-extracted. Therefore, most frequently, another analytical step is needed, i.e. extract purification. Saponification, gel permeation chromatography (GPC), sulphuric acid treatment, adsorption chromatography (alumina, silica gel, *Florisil*) were reported by many cited below authors to have been used alone or in combination with other techniques to remove interfering compounds.

Acid digestion or saponification is a destructive method for the removal of lipids that is commonly applied for this purpose; for example lipid removal with sulphuric acid treatment after USE (Lambropoulou, Konstantinou, & Albanis, 2006), Soxhlet extraction (Falandysz et al., 2004) or MSPD (Valsamaki, Boti, Sakkas, & Albanis, 2006). Sulphuric acid-impregnated silica gel columns have also been used for the restructive removal of lipids from food samples (Dionex Application Note 316, 2000).

The most commonly used method of purification is adsorption chromatography applying the SPE technique (Żwir-Ferenc & Biziuk, 2004). However, column chromatography using alumina, silica gel and *Florisil*, or a combination of these adsorbents, cannot always guarantee lipid-free extracts. This technique has been successfully applied to the analysis of contaminants in several food matrices, including: PCB in fish (Agustin, Park, Hong, Ryu, & Lee, 2005), organochlorine pesticides in sesame seeds (Papadakis, Vryzas, & Papadopoulou-Mourkidou, 2006) and phenylurea herbicides in potatoes (Escuderos-Morenas et al., 2003).

Gel permeation chromatography is generally recommended for purifying extracts obtained from biological samples; it can be used for separating large molecules (e.g., lipids), because its principle of operation is based on size exclusion. This method can be employed for purifying extracts of many pesticides and PCBs, resulting in products that are ready for further analysis by means of gas or liquid chromatography with a proper detector (Liu et al., 2007). Because of its properties, GPC has mainly been applied to purify fat-rich extracts, such as extract from avocado (Fernandez Moreno, Arrebola Liebanas, Garrido Frenich, & Martinez Vidal, 2006), olive oil (Guardia-Rubio, Fernandez-De Cordova, Ayora-Canada, & Ruiz-Medina, 2006), poultry, pork and lamb meat (Garrido Frenich, Martinez Vidal, Cruz Sicilia, Gonzalez Rodriguez, & Plaza Bolanos, 2006), but suffers drawbacks because it requires special equipment for a forced liquid flow.

Table 5
Techniques of sample extraction and purification (Ahmed, 2003; Tekel et al., 2001; Żwir-Ferenc and Biziuk, 2004)

Technique	Extraction	Purification	Short characteristics
LLE	++	–	Laborious, highly time-consuming, large solvent volume, purification step needed
Soxhlet and Soxtec extraction	++	–	Laborious, highly time-consuming, large solvent volume, no filtration required
FMASE	++	–	Purification step needed, low solvent volume, but solvent must be able to absorb microwaves
USE	++	–	Purification step needed, large solvent volume
MAE	++	–	Purification step needed, low solvent volume, but solvent must be able to absorb microwaves, evaporated temperature
ASE	++	–	Purification step needed, low solvent volume, evaporated temperature
SFE	++	+	Many parameters to optimize, decreased or no use of solvents, evaporated temperature, concentrated extracts
Membrane extraction techniques	++	+	Easily automated, decreased or no use of solvents, direct introduction of untreated samples, highly time-consuming
SPE	++	+	Easily automated, low solvent volumes,
SPME	++	–	Decreased or no use of solvents, easily automated, no sensitivity to suspended matter, problems with reproducibility and optimization
MSPD	++	+	Low solvent volume, not very suitable for dry samples or samples with high lipid content – adsorbent consumption is then relatively high and MSPD requires an additional clean-up step
SBSE	++	–	Significant increase in the amount of extracting medium (PDMS) as compared to SPME, which results in a very high degree of recovery
GPC	–	++	Easily automated, long lifespan of columns, good recovery, highly time-consuming
Sulphuric acid	–	++	Destructive method for the removal of lipids, good recovery
Saponification	–	++	Destructive method for the removal of lipids, fair recovery

++ main application, + secondary application, – generally no application.

In order to reach a higher sample throughput, Focant et al. (Focant, Eppe, Pirard, & De Pauw, 2001) replaced slow GPC purification with high-capacity disposable silica (HCDS) columns containing 28 g of acidic, 16 g of basic, and 6 g of neutral silica; this allowed up to 4 g of lipids for each sample to be retained. The HCDS column is added to the classic set of columns and is the first one in contact with the sample. Such a column system has found application in purifying extracts from samples characterized by a high lipid content, e.g., poultry, fish and eggs.

When analysing the techniques for determining pesticides and PCBs in food, it can be concluded that a single, universal procedure, applicable to all types of samples, does not exist. Because a combination of different techniques is often required, the aim of any analytical procedure should be achieved in as few steps as possible (Biziuk, 2001). Information on the methodology used for determining pesticides and PCBs in various foods are presented in Table 5.

4. Conclusions

Although detection techniques are becoming more specific and sensitive, there is still a need for good sample preparation methods which are compatible with modern analytical techniques. The development of more selective extraction and purification techniques that can be applied to complex matrices, such as food, will enable analysis at the low levels now required by legislation for many contaminants, but more importantly, result in methods which produce more reliable data to support food safety risk assessments. Modern sample preparation techniques should be not only simple, reliable, cheap and take into account chemical laboratory waste problems, but also must be similar to common analytical techniques, in order to minimize errors and develop expert systems that work without staff supervision. For these reasons, modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation, and the minimalization of sample size and organic solvent used.

Although many achievements in the development of new sample extraction, enrichment and purification techniques, the applicability of some of these techniques for trace level contaminants in foods is still in question.

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