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# Modern Extraction Techniques for Pesticide Residues Determination in Plant and Soil Samples

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## 1. Introduction

Due to intensive use of pesticides, their residues have become an unavoidable part of the environment, and they are often detected in all environmental segments and therefore their monitoring has been frequently performed throughout the world.

As the presence of trace amounts of both pesticide residues and their degradation products could be potential health hazards, UN organization has formed specialized groups: World Health Organization (WHO) and Food Agriculture Organization (FAO), with the aim to establish restrictive measures to protect the environment against pollution. These organizations and their experts groups on annual meetings summarize international achievements in pesticides domain, establish legislation and make recommendations obligating member states to act in accordance with international standards.

As pesticides are a very heterogeneous group of compounds with different biological and physicochemical properties, the current trend in pesticide residues analysis is developing multi-residual methods that not only provide simultaneous determination of large number of pesticides, but also can be applicable to large numbers of samples of different origin.

Although separation chemical analysis involves several stages (sample preparation, analyte separation i.e. quantification and data analysis), sample preparation step can be marked as "the most critical" one. Traditional sample preparation methods (liquid-liquid extraction, Soxhlet extraction, etc.) are laborious, time consuming, expensive, requires large amounts of organic solvents and usually involve many steps, leading to loss of some analyte quantity. Additionally, consequences of hydrocarbon solvents use, such as ozone depletion and generation of considerable cancer waste, lead to reduction of not only their use but also their manufacture. As a result, modern sample preparation procedures, such as accelerated solvent extraction (ASE), supercritical fluid extraction (SFE), microwave assisted extraction (MAE), solid phase extraction (SPE), solid phase microextraction (SPME), matrix solid phase dispersion (MSPD) extraction and QuEChERS (quick, easy, cheap, effective, rugged and safe), have been developed to overcome the drawbacks of the traditional approaches. It should be indicated that SFE, ASE and MAE are instrumental techniques, and often use SPE and SPME for purification of obtained extracts, and also its concentration in case of SPME.

Overall, a comprehensive analytical procedure is carried out in the way that obtained results can be found within prior established concentration range. Whether the measurement will

be performed at the desired concentration range is determined by the instrument sensitivity and the choice of sample preparation method. Multiple factors, related to the physical properties of not only tested active ingredients (volatility, solubility in water and organic solvents, stability, acid-base properties, etc.), but also sample matrix (water, lipids, pigments content etc.), must be considered during an experiment planning. The choice of sample treatment depends directly on mentioned factors, but also on analysis purpose i.e. on required detection method sensitivity (limits of detection) and quantification accuracy (whether the aim is to establish the exact concentration value regardless maximum residues limits (MRLs), or just to establish if result is above or under MRLs). Considering complexity of these issues, analytical procedure for each specific case should be chosen in order to minimize problems relating to analysis duration, consumption of solvents and other necessary reagents, and also to reduce number of involved analytical steps, which would minimize potential sources of errors. Additionally, it is desirable that chosen analytical procedure allows the simultaneous determination of large number of pesticides.

This paper describes the basic principles of modern extraction techniques, comparing their advantages and drawbacks, and their ability and applicability for pesticide residues determination, with special emphases on plant material and soil samples.

## 2. Supercritical fluid extraction (SFE)

This technique uses supercritical fluid (SF)<sup>1</sup> as an extraction tool for "drawing out" the organic compounds from solid matrices. Commonly used for this purpose is CO<sub>2</sub>, as it has relatively low critical temperature (31<sup>0</sup> C) and low critical pressure (73 kPa) (Atkins & De Paula, 2002), it is not reactive and is accessible in a high degree of purity at low cost. Changes in temperature and pressure at which the supercritical CO<sub>2</sub> is held will increase or decrease the "strength" of solvent and thus the selectivity of extraction performed. At constant temperature which exceeds critical temperature, the supercritical CO<sub>2</sub> will be able to extract analytes of low polarity at low pressure, and high polarity analytes at high pressure. SFE with CO<sub>2</sub> is usually performed at pressures that are not high enough to achieve efficient extraction of polar compounds. In such conditions, the supercritical CO<sub>2</sub> is a good extraction medium for non-polar compounds and moderately polar ones, such as PAHs, PCBs, organochlorine (OCPs) and organophosphorus (OPPs) pesticides, etc.. The efficiency of supercritical CO<sub>2</sub> can be improved by adding small amounts of modifiers, which identity is often more important than their concentration, since the major role of a modifier is to interact with the sample matrix to promote desorption into the fluid (Langenfeld et al., 1994). Some of the common solvents such as acetone (Valverde-García et al., 1996; Kaihara et al., 2002; Ono et al., 2006) and methanol (Valverde-García et al., 1996; Rissato et al., 2005a, 2005b) are now mostly used as

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<sup>1</sup> Supercritical fluid is a fluid held at temperature and pressure close to but somewhat larger than its critical values. Under these conditions, the fluid shows rapid diffusivity and viscosity that are typical for the gas phase, but also solvation properties (moistening) that is characteristic of a liquid. Properties similar to gas phase allow the fluid to penetrate into the sample and to establish contact with the analytes much faster than the liquid solvent does. When the mentioned contact is established, the extraction process depends on the solvation abilities of the fluid to release the analytes from the adsorption centers of the sample.

modifiers. Besides CO<sub>2</sub>, supercritical N<sub>2</sub>O has been much in use as well, and it could be used both with and without modifiers.

The basic principles and possibilities of applying the SFE technique for determining pesticide residues in samples of different origin can be found in the reports generated by Gilbert-Lopez et al. (2009); Sunarso & Ismadji (2009); Rissato et al. (2005a, 2005b); Motohashi et al. (2000) and Torres et al. (1996).

In general, SFE usually lasts less than two hours, and the further analysis can be accomplished in several ways. According to one, SF with analytes is passed through a capillary that is immersed in an appropriate solvent. While in the capillary, SF exists, but after leaving the capillary it becomes a gas (the pressure falls below the critical pressure). The largest part of this gas passes through the solvent, while the extracted analytes are retained in the solvent (the degree of retention depends on the solvent, i.e. the solubility of the analyte in it). Read phonetically Also, the flow of SF can be directed to a solid sorbent, which will then bind analytes, and its elution by appropriate solvent, analysts translate into a solution suitable for further analysis. Also, the flow of SF could be directed directly to capillary column of the gas chromatograph (GC), thus obtaining the "on-line" SFE. This approach enables analytical scheme with the highest sensitivity for a limited amount of sample available for analysis.

The recent studies have shown that SFE methods, followed by additional purification of the obtained extracts, meet the strict criteria of the pesticide residues analysis. Thus, Ono et al. (2006) showed that SFE method combined with purification on the SPE columns (C18 and Envicarb/NH<sub>2</sub>), could be used for determination of 242 pesticides in spinach, 245 in green beans and 263 in orange. Rissato et al. (2005a) concluded that the SFE preparation of potato, tomato, lettuce and apple samples, combined with the extracts cleanup on amino propylene columns, could be used for determination of 37 pesticides. Kaihara et al. (2000, 2002) have developed the SFE method that combined with the purification on PSA and florisil columns may be used for determination of 27 pesticides in cucumber, potato, radish, apple, banana and rice samples. Norman & Panton (2001) have developed the SFE method for determination of OPPs in wheat and maize using GCB (graphitized carbon black), and Quan et al. (2004) found out that SFE of ginseng followed by purification on C18, gave satisfactory results in determining OCPs. The same sorbent was shown to be the best choice for determination of 32 pesticides in soil using SFE sample preparation (Rissato et al., 2005b).

### 3. Solid phase extraction (SPE)

SPE is one of the most commonly used sorbent techniques in analyzing pesticide residues. This method is based on the omission of extracts containing target analytes through a column filled with the appropriate sorbent (which was previously conditioned by an appropriate solvent or solvent mixture), or passing of an appropriate solvent through the SPE column to which a suitable amount of sample was previously added. Using selective solvents, first the coextractants from the SPE column can be successfully eluted, and then the target analytes (Figure 1, A), or the elution of analytes can be direct, where undesirable coextractants derived from the sample matrix remain in the SPE column (Figure 1, B).

Compared with the traditional methods, SPE has many attractive features. It is easy to operate, costs less, it has been automated and uses small amounts of solvent. SPE is the multifunctional techniques, since the purification and the concentration occur in the same step. Unfortunately, SPE has certain limitations, primarily related to lower yields (recovery),

i.e. slightly lower sensitivity, in situations where there is "clogging" of the SPE column (blocking of the sorption centers by solid and oily components originating from the sample).

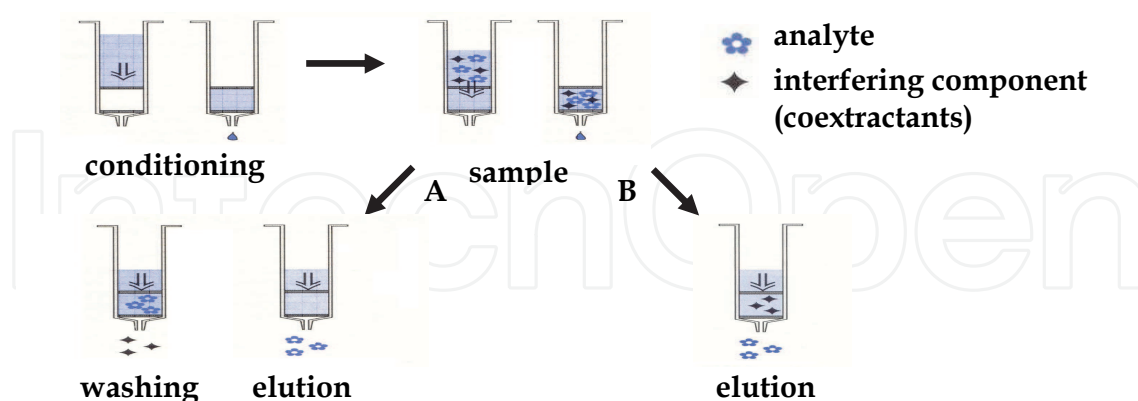


Fig. 1. The basic principle of SPE technique

The most commonly used SPE sorbents in pesticide residues determination are: reverse-phase octadecyl (C18), normal-phase aminopropyl (-NH<sub>2</sub>) and primary-secondary amine (PSA), anion-exchanger three-methyl ammonium (SAX) and adsorbents such as graphitized carbon black (GCB). Normal-phase sorbents such as florisil (MgSiO<sub>3</sub>), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) and silica (SiO<sub>2</sub>) are usually used in combination with the previously mentioned sorbents. The SPE cartridge should be chosen depending on the physicochemical properties of pesticides that are searched for in a particular sample, and the nature of the sample matrix. For instance, the researches indicate that the GCB sorbent is suitable for extraction of compounds of different polarity, and that it causes retention of pigments (carotenoids and chlorophylls) and sterols, and now are widely used for purification of plant extracts (Schenck et al., 2002; Anastassiades et al., 2003). On the other side, PSA sorbent proved to be effective in removing polar compounds and fatty acids, while the SAX is suitable for the removal of fatty and other organic acids and sugars (Okimashi et al., 2005). Activated charcoal proved to be a good solution for removal of pigments from tomato extracts (Kaipper et al., 2001), and cabbage and carrots (Wang et al., 2008), while the florisil gave good results in pyrethroids determination in lettuce, cabbage, cauliflower, carrot, green pepper and green beans (T. Chen & G. Chen, 2007), and metribuzin and quizalofop-p-ethyl in potato and soil samples (Hu et al., 2010). Diatomaceous earth was a good solution for neonicotinoids determination in apricot, peach, pear, celery and courgette (Di Muccio et al., 2006), and C18 cartridges for determination of various pesticides in strawberry, grape, lettuce, tomato (Juan-García et al., 2005) and carbamates in soil (Santalad et al., 2010). Silica gel is effective in determination of OCPs in soil samples (Lehnik-Habrink et al., 2010).

The most of the SPE methods are based on a combination of two or three cartridges. As GCB is suitable for removal of lipids, waxes and other nonvolatile, non-polar coextractants with high molecular weight, it is usually used in combination with other sorbent. Thus, Pang et al. (2006) used SPE for determination of 446 pesticides in cabbage, tomato, cucumber, spinach, cauliflower, celery, peas, carrots, potatoes, lettuce, onion and leek, and found out that the C18/GCB/-NH<sub>2</sub> combination was the best. Except for slightly lower recoveries obtained for onion and leeks, the method was shown as good choice for all other samples. Okimashi et al. (2005) tested SPE methods by determining 180 pesticides in tomato, lettuce,



pepper, broccoli, spinach, orange, apple and banana, and found out that the PSA/GCB combination was the most effective. The same combination proved to be a good solution for determination of 23 pesticides in lettuce, chard and spinach (González-Rodríguez et al., 2008), while Tao et al. (2009) used a GCB/ $\text{Al}_2\text{O}_3$  combination in the analysis of cucumber and cabbage, and obtained satisfactory results for 39 pesticides (carbamates, pyrethroids, OCPs and OPPs). The SAX/PSA combination was a good solution for pyrethroids and OCPs determination in grape, orange, tomato, carrot and green mustard (Sharif et al., 2006).

#### 4. Solid phase microextraction (SPME)

Solid phase microextraction, one of the newest extraction techniques, is widely used in the pesticide residues analysis in samples of different origin, due to the fact that purification and concentration of the sample extract (analytes of interest) are running simultaneously.

The basic part of the SPME system is SPME syringe that visually resembles on the chromatographic, except for the fact that it contains a 1 cm long fiber located within a syringe needle, which is made of an appropriate polymer deposited on the holder of fused silica. Microextraction process is based on the redistribution of analytes between microextraction fiber and sample matrix, i.e. on the selective sorption of target analytes in the active layer of the fiber and direct desorption in the chromatograph injector (thermal in the case of the GC, i.e. by solvent elution in the case of LC - liquid chromatography). The basic principle of analytes microextraction from the solution is shown in Figure 2.

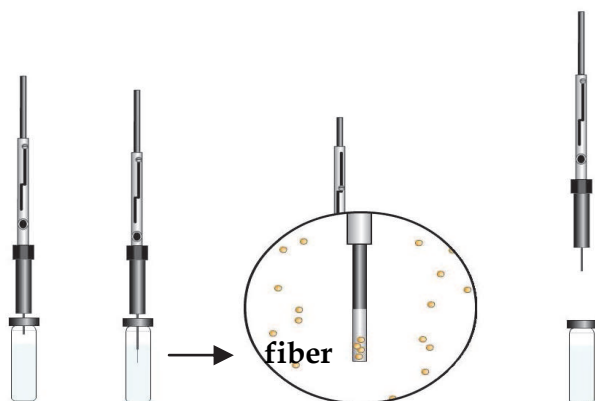


Fig. 2. Procedure for microextraction of analytes from solution

Before the analysis, the fiber is drawn into a metal tube of the SPME syringe. After breaking through the vial septum in which a certain sample amount was previously inserted, the fiber is pulled out from the syringe i.e. it is exposed to the sample by lowering the syringe plunger. After specific time, the fiber with the sorbed analytes is drawn into the needle, which is then pulled out from the vial. Analytes desorption from the fiber is performed by introducing a SPME syringe needle into the injector of the chromatographic system.

SPME is an equilibrium technique, where analytes are distributed between the three phases: sample, gas phase and fiber. The fiber does not extract all analytes present in the sample, but by the proper calibration, this technique can be used for successful quantification (Đurović et al., 2007a; Pawliszyn, 1997). The amount of analytes that would be adsorbed on the fiber will depend on the thickness and polarity of the active fiber layer, sampling mode (direct sampling - microextraction from solution, »DM-SPME« and headspace sampling -

microextraction from gas phase, »HS-SPME«), the nature of the sample and the analyte (analyte polarity, its molecular weight, pH value, nature of matrix), the mode and speed of the sample mixing, the SPME duration, the temperature at which it is performed, and so on. Today, about thirty different fiber types are in use (different types of polymers and their thickness), so when selecting the fiber it is necessary to take into consideration several factors: molecular weight, structure and polarity of the analyte molecules, the polarity of fibers, the mechanism of extraction (used sampling mode), the detection limit and range of linearity that is desired to be achieved. In order for a fiber to extract specific compounds from a given matrix, it must have a much higher affinity for the given analytes than a matrix, where the general rule applies: non-polar analytes are more efficiently extracted by non-polar active fiber layer, i.e. polar by polar. The research in the field of pesticide residues has indicated that, in the most of the cases, fibers with extremely non-polar polydimethylsiloxane (PDMS) and highly polar polyacrilate (PA) active layers are most effective in the analysis of samples of different origin (Doong & Liao, 2001; Sakamoto & Tsutsumi, 2004; Đurović et al., 2007b, 2007c, 2010b; Fernandez-Alvarez et al., 2008). After fiber selection, it is necessary to determine optimal conditions for analytes transfer in the chromatographic system. Adsorbed analytes are desorbed from the fiber by introducing the SPME syringe needle into the injector. Defining the parameters of desorption involves determination of the optimal injector temperature, flow of the carrier gas and desorption time in the case of GC, i.e. proper choice of elution solvent, its flow rate and desorption time, in the case of HPLC.

Although the maximum of SPME sensitivity is achieved at equilibrium times, for practical reasons, extraction time can be shortened (Đurović et al., 2007a, 2010a, 2010b; Pawliszyn, 1997). The most effective ways to overcome the kinetics restrictions are heating and efficient sample mixing. The temperature has two opposite effects. On one side, it increase increases the analytes transfer from the sample to the fiber, while on the other side, due to the simultaneous heating of the fiber during extraction, there is enhanced desorption of analytes from it. Therefore, the necessary step in method development is optimization of the extraction temperature. The speed of extraction is also determined by the sample stirring efficiency. Intensive stirring increases the analytes mobility, and therefore reduces the equilibrium time and increases the analytes amount adsorbed on the fiber. However, in method developing it should be noted that the sample stirring leads to its warming, which may also have non-preferred effects, especially in the case of direct mode.

The matrix nature greatly influences the SPME efficiency, too. Since the analytes distribution coefficients are partially determined by analytes/matrix interaction, appropriate matrix modification can increase the analytes partition coefficients. Thus, for example, the presence of chloride and sulfate ion increases the ionic strength of the solution, which makes a large number of compounds less soluble. In this way, by weakening the matrix/analyte interaction, distribution coefficients can be significantly increased (Arthur et al., 1992).

Considering the fact that SPME is a single-stage method that does not require additional purification and concentration of the sample, the problems related to the matrix occur in the analysis of samples with complex matrices. The researches have shown that the negative effect of the matrix could be significantly reduced by adequate dilution of the sample with the distilled water (Simplicio & Boas, 1999; Đurović et al., 2005, 2007c, 2008).

There are a significant number of SPME applications in pesticide residues analysis. In most cases, SPME method was based on the analysis of sample mixture with water, regardless of whether the extraction medium was placed directly into the formed suspension (Berrada et al., 2004; Beltran et al., 2003; Đurović et al., 2007c, 2010b), or the sampling was done from the

gaseous phase (Chai & Tan, 2009; Kin & Huat, 2010; Zhao et al., 2006; Lambropoulou & Albanis, 2003; Fytianos et al., 2006). However, quite a number of researchers opted for methods based on SPME determination of pesticides combined with the extraction of samples with organic solvent or solvent mixture, and the corresponding dilution of extract obtained with water (Wennrich et al., 2001; Ravelo-Pérez et al., 2008; Parrilla Vázquez et al., 2008; Đurović et al., 2007c, 2010a, 2010b; Herbert et al., 2006; Vega Moreno et al., 2006). Majority of these methods include adjustment of the ionic strength of solution (Berrada et al., 2004; Beltran et al., 2003; Kin & Huat, 2010; Chai & Tan, 2009; Đurović et al., 2010a, 2010b; Zhao et al., 2006; Filho et al., 2010; Lambropoulou & Albanis, 2003; Fytianos et al., 2006; Đurović et al., 2009), and some of them adjustment of the pH value (Berrada et al., 2004; Ravelo-Pérez et al., 2008; Parrilla Vázquez et al., 2008; Filho et al., 2010;) prior to SPME analysis.

The research results indicate that the most often used SPME fibers in the pesticide residues analysis (PDMS and PA) are a good choice for determination of: phenyl urea in carrot, onion and potato (Berrada et al., 2004); OCPs in soils (Zhao et al., 2006; Herbert et al., 2006); OPPs in strawberries and cherries (Lambropoulou & Albanis, 2003) and samples of banana, apple, grapefruit, orange, lemon, kiwi, pineapple, pear, peach, apricot, grapes, melon, lotus, plum, mango, cherry and coconut (Fytianos et al., 2006); OCPs and OPPs in cucumber and strawberry (Kin & Huat, 2010); pesticides belonging to different chemical groups in tomato and cucumber (Chai & Tan, 2009), mango (Filho et al., 2010), soil (Đurović et al., 2010a, 2010b), i.e. in samples of potato, tomato, onion, cabbage and pepper (Marković et al., 2010).

Considering that in the SPME analysis only 1 cm of fiber is exposed to the sample, not only the nature, but also the size of the active surface layer will significantly affect the microextraction efficiency. Thus, by adding an additional material into the active layer of the fiber, its outer surface may increase, and therefore often the SPME efficiency, too. On the other side, the added material can significantly change the polarity of the fiber (similar to the GC stationary phase). Thus, for example, by using mixed PDMS/DVB (polydimethylsiloxane/divinyl-benzene) fiber, Beltran et al. (2003) provided satisfactory analytical parameters for SPME determination of pyrethroids in tomato samples; Wennrich et al. (2001) for determination of OCPs in kohlrabi, lettuce and tomato; Parrilla Vázquez et al. (2008) for determination of pyrethroids in cucumber; Vega Moreno et al. (2006) for determination of OCPs in soil, while Ravelo-Pérez et al. (2008) developed a method for determination of pesticides belonging to different chemical groups in tomatoes.

## 5. Microwave-assisted extraction (MAE)

Microwave-assisted extraction (MAE) is a technique based on usage of the microwave energy, and where compounds can be extracted more selectively and rapidly, with similar or better recovery compared to conventional extraction processes.

The MAE effects a direct migration of the desired components out of the matrix, as a result of selective energy application into the matrix. High method efficiency is a result of the matrix macrostructure destruction (Lambropoulou et al., 2007). During the MAE of plant material, microwave rays travel freely through the solvent and interact selectively with the free matrix water causing localized heating. The result is non-uniform temperature rise with more pronounced effects where the free water is in larger proportions. The result is a volume expansion within the systems. The walls of these systems cannot accommodate the high internal pressures and rupture spontaneously, allowing the organic contents to flow freely toward the relatively cool surrounding solvent that solubilizes them rapidly (Paré &



Belanger, 1994). Considering the complexity of plant material and its non-uniformity regarding different amount of free water, the MAE advantage can be noticed. Particularly, by providing different microwave energy levels, it is possible to selectively rupture some systems over others, thus it is possible to develop schemes that will effect the selective extraction of the given systems contents. MAE is also a promising technique for soil samples, particularly owing its possibility to control temperature, pressure and microwave energy, as well as to perform a few extractions simultaneously (Ranz et al., 2008).

For method optimization, several variables such as volume and solvent composition, extraction temperature and time, are usually studied. In order to heat a solvent, part of it must be polar with high dielectric constant to absorb microwave energy efficiently. Non-polar solvents with low dielectric constants can be also used, by adding certain amount of polar solvent that absorbs the microwave radiation and passes it on to other molecules (Caddick, 1995). For example, hexane and toluene can be modulated by the addition of small amounts of acetone or methanol (Ericsson & Colmsjö, 2000).

The first use of MAE technique for pesticide residues determination (parathion and bromophos in maize, soya bean, fava bean, walnut, cotton seed and soil), was reported by Ganzler et al. (1986). In 1993, Onuska & Terry evaluated the extractability of various pesticides in sediment samples, and in the same year Steinheimer (1993) extracted atrazine from soil samples. These works were followed by an extensive paper by the group of Lopez-Avila (1994), presenting procedures for extraction of organic compounds such as OCPs, among others, from soils and sediments. In 1997, Pylypiw et al. used a MAE for determination of several pesticides in beet, cucumber, lettuce, pepper and tomato. The results show that MAE is a viable alternative for determination of atrazine and OPPs in orange peel (Bouaid et al., 2000), carbendazim, diethofencarb, azoxystrobin, napropamide and bupirimate in strawberries (Falqui-caio et al., 2001), fenitrothion in beans (Diagne et al., 2002) and pyrethroids in strawberries (Sanusi et al., 2004). Application of MAE for extraction of acetamiprid from cabbage (Pritam & Mukherjee, 2010) and thiophanate methyl and carbendazim from cabbage and tomatoes (S.B. Singh et al., 2007) are also reported. MAE was also carried out for the determination of thiamethoxam, imidacloprid and carbendazim in cabbage, tomatoes, chilies, potatoes and peppers (S. B. Singh et al., 2004). Barriada-Pereira et al. (2005, 2007) described it as a satisfactory method for OCPs determination in legume vegetation and horticultural samples (lettuce, tomato, spinach, potato, turnip leaf and green bean). Likewise, Paíga et al. (2009) used the MAE method for quality control vegetable samples of zucchini, cucumber, lettuce and pepper, i.e. for determination of carbamates and urea pesticides, while El-Saeid & Al-Dosari (2010) applied MAE technique in monitoring of insecticide (OCPs, OPPs, pyrethroids), fungicides, acaricides and herbicides in Riyadh dates. In 1994, 20 OCPs were extracted from six marine sediments and soils (Lopez-Avila et al., 1994), and in a subsequent study the list of compounds was expanded to nearly a hundred OCPs and OPPs (Lopez-Avila et al., 1995). Investigations on MAE extractions of OCPs and OPPs from soil, optimization and comparison of method, was performed by numerous authors in years to come (Concha-Graña et al. 2003; Fuentes et al., 2007; W. Wang et al., 2007). MAE determination of triazines in soils was first reported in 1993 (Steinheimer), followed by Hoogerbrugge et al. (1997) work. MAE determination of imidazolinone herbicides have been reported by Stout et al. (1996, 1997). Other investigated herbicides are sulfonyl- and phenylurea herbicides (Font et al., 1998; Molins et al., 2000). The investigated fungicides were hexaconazole (Frost et al., 1997), and dimethomorph (Stout et al., 1998), both extracted from soils. De Andréa et al. (2001) applied MAE for determination of methyl

parathion, p,p'-DDE, HCB, simazine and paraquat dichloride in soil, Sun & Lee (2003) for carbamates in soil, and Paíga et al. (2008) for 8 pesticides in the same matrix type.

From economical and practical aspects, MAE is a strong competitor to other recent sample preparation techniques. The main MAE advantages are the low temperature requirement, high extraction efficiency, complete automation, and the possibility of extracting different samples at the same time without interference. The main disadvantage of MAE seems to be the lack of selectivity resulting in the co-extraction of significant amounts of interfering compounds. Additional cleanup is therefore needed before chromatographic analysis. Apart from that, the poor efficiency of microwaves when either the target compounds or the solvents are non-polar, or when they are volatile, can be regarded as another disadvantage. Besides, it is important to notice that the application of microwave energy to flammable organic compounds, such as solvents, can pose serious hazards in inexperienced hands, thus an extraordinary level of safety and attention to details when planning and performing experiments must be used by all personnel dealing with microwaves.

## 6. Accelerated solvent extraction (ASE)

Accelerated solvent extraction (ASE), also known as pressurized liquid extraction (PLE), is relatively new sample preparation technique, that uses small amounts of water and organic solvents, and is based on the extraction under elevated temperature (up to 200 °C) and pressure (up to 20 MPa) for short time periods, resulting in better extraction efficiency.

In practice, a used solvent is pumped into an extraction cell containing the sample, which is then brought to an elevated temperature and pressure. Later, the extract is transferred to a collection vial for cleanup and analysis. At high temperatures, viscosity and the surface tension of the solvent decrease, resulting in a substantial extraction rate increase (Anastassiades et al., 2003). The solvent is kept below its boiling point by applying high pressure that forces its penetration into the sample. The combination of high temperature and pressure results in better extraction efficiency, thus minimizing solvent use. The extraction efficiency is almost independent of sample mass, i.e. is mainly dependent on temperature (Richter et al., 1996; Smith, 2002). Besides the type of the solvent used, the main parameters which influencing ASE efficiency are extraction temperature and time (Luo et al., 2010). Although high temperatures increase the efficiency, it may lead to degradation of thermally labile compounds, and to the co-extraction of interfering species. Hence, a compromise between the extraction efficiency and minimization of interfering compounds must be performed carefully, and in addition, usually a further clean-up step involves.

ASE has been successfully used for pesticides determination in samples of different origin. Thus, Di Muccio et al. (2006) developed ASE method for neonicotinoids determination in apricot, peach, pear, celery and zucchini. Richter et al. (2001) developed ASE for OPPs determination in carrot, Wennrich et al. (2001) for OCPs in strawberry, apple, lettuce, tomato and kohlrabi, while Cho et al. (2008) tested ASE for determination of iprodione, chlorpyrifos-methyl and endosulfan in kiwi. In 2007, Barriada-Pereira et al. described it as a satisfactory method for determining 21 OCPs in lettuce, tomato, spinach, potato, tomato and bean, and in the same year Carabias-Martínez et al. (2007) used ASE to determine triazines in potato, carrot, lettuce, bean, zucchini and orange. ASE was also used for determination of 28 pesticides in pear, potato and cabbage (Adou et al., 2001). In subsequent studies, this list was expanded to 74 pesticides extracted from cucumber, lettuce and tomato (Garrido

Frenich et al., 2005), and up to 130 pesticides extracted from oranges, nectarines and spinach (Cervera et al., 2010). A group of authors managed to extract 29 carbamates from dried fruits (raisin, prune and mango), spices (turmeric, masala, sage, thyme and red pepper) and from soybean paste and soy sauce (Terada et al., 2008), while Gilbert-López et al. (2009) indicated ASE application for pesticide from fatty vegetable matrices. Lehotay et al. (2005, 2005a) reported ASE method for 229 pesticides determination in various fruits and vegetables. ASE efficiency was also confirmed for atrazine and alachlor determination in soil (Gan et al., 1999), as for the arylphenoxypropionic herbicides (Marchese et al., 2001). ASE was carried out for determination of DDT and its metabolites (Tao et al., 2004), i.e. abamectin in soil samples (Brewer et al., 2004). ASE methods for soil samples were reported for OCPs (W. Wang et al., 2007), for bromacil and diuron (Pinto & Lanças, 2009), and dichlorvos, dimethoate, parathion, malathion and chlorpyrifos determination (J. S. Zhang et al., 2010). Obvious ASE advantage is that it requires much less solvent and shorter extraction times than conventional techniques. Using elevated temperatures and pressures with organic solvents, an enhanced analytes extraction can be achieved. Additionally, ASE is reduced both, waste levels and analysts exposure to harmful solvents. However, samples with high moisture contents require desiccation before the extraction step (Cervera et al., 2010).

## 7. QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method

Despite mentioned disadvantages related to conventional solvent extraction (SE) methods, they are still the most popular methods for routine analysis. To overcome the SE drawbacks, new trends in pesticide residues analysis have appeared. A good example of this is the QuEChERS method (Anastassiades et al., 2003). The authors questioned the conditions previously used for pesticide residues analysis, and through extensive experiments and novel use of  $\text{MgSO}_4$  for salting out extraction/partitioning and dispersive solid-phase extraction (d-SPE) for cleanup, they devised a highly streamlined sample preparation method with excellent results for a wide range of pesticides in many types of samples.

The original procedure consists in the sample extraction by hand-shaking or vortex mixing with the 10 mL of acetonitrile (MeCN). Gram quantities of salts (4 g of  $\text{MgSO}_4$  and 2 g of NaCl) are then added to the sample by mixing, to drive analytes partitioning between the aqueous residue and the solvent. After vortex mixing and centrifugation, clean-up and removal of residual water is performed using a d-SPE procedure (PSA adsorbent and anhydrous  $\text{MgSO}_4$  are mixed with the sample extract), that requires less time than the traditional SPE and simultaneously removes residual water and many polar matrix components, such as organic acids, some polar pigments, and sugars.

As a polar solvent, miscible with water, with sufficient dispersive (hydrophobic) properties to extract effectively both polar and non-polar pesticides, MeCN is chosen as the QuEChERS solvent. Use of this solvent in the QuEChERS method proved to be successful for extraction of several pesticides classes from different matrices (Anastassiades et al., 2003; Asensio-Ramos et al., 2010; Drozdzyński & Kowalska, 2009; Lehotay et al., 2005, 2005a, 2005b; X. Li et al., 2010; Rashid et al., 2010; Shi et al., 2010; Yang et al., 2010; Đurović & Đorđević, 2010c, 2010d).

Studies showed that some pesticides gave lower recoveries depending on pH of the matrix (Anastassiades et al., 2007; Lehotay et al., 2005, 2005a). Anastassiades et al. (2007) realized that buffering at pH=5 during extraction gave the optimum balance to achieve acceptably recoveries (>70%) for pH-dependent pesticides, independent of the matrix. On the other hand, Lehotay (2007) modified the method to use even stronger acetate buffering conditions.

Both versions of methods went through extensive laboratory trials and successfully met statistical criteria for acceptability by independent scientific standards organizations. So the acetate-buffering version becomes AOAC Official Method 2007.01 (Lehotay, 2007) and the citrate-buffering version being named as Standard EN 15662 Method ([www.cen.eu](http://www.cen.eu)).

There is an abundance of the QuEChERS applications for pesticides determination in different plant samples. Thus, for example, QuEChERS provides satisfactory results for determination of 229 pesticides in lettuce and orange (Lehotay et al., 2005), 109 in rice (Thanh et al., 2007), 160 in tomato, pear and orange (Kmellár et al., 2008), 140 in cucumber and orange (Fernández Moreno et al., 2008), 118 in vegetables juice (Nguyen et al., 2009), 138 in apples, bananas, pears, apple juice, peas, creamed corn, squash and carrots (J. Wang & Leung, 2009), 150 in tomato, strawberry, potato, orange, and lettuce (Koesukwiwat et al., 2010), 300 in tomato, apple, lettuce, cucumber, carrot, mushroom, grapes, lemon, pepper, pear, potato and cabbage (Kmellár et al., 2010), 69 in zucchini, melon, cucumber, tomato, garlic, lettuce and pepper (Camino-Sánchez et al., 2010), 46 in onion, spinach, potato, carrot, cucumber, cabbage and tomato (Srivastava et al., 2010), 150 in grapes (Afify et al., 2010), 148 in onion, spinach, potato, carrot, peas and tomato (J. Wang et al., 2010), 73 OPPs and carbamates in rice, tree nuts and citric fruits (Chung & Chan, 2010) and 14 OCPs in apricot, plum, cherry, nectarine, pear and apple (Cieślik et al., 2011). Besides, QuEChERS has been successfully used for determination of metaflumizone (Dong et al., 2009), azadirachtin, spinosad, rotenone (Drozdzyński & Kowalska, 2009), oxadiazyl (Shi et al., 2010) and 38 pesticides (Yang et al., 2010) in soil samples. As a modified version, it was applied for OCPs (Rashid et al., 2010) and OPPs determination in soil samples (Asensio-Ramos et al., 2010).

The QuEChERS advantages are the high recovery, accurate results, low solvent and glassware usage, less labor and bench space, lower reagent costs, and ruggedness. The main QuEChERS disadvantage is that the final extract must be concentrated to furnish the necessary sensitivity i.e. to achieve the desired limits of quantification (LOQ).

## 8. Matrix solid phase dispersion (MSPD)

Matrix solid-phase dispersion (MSPD) is a new SPE-based extraction and clean-up technique developed for pesticide multi-residue analysis (Kristenson et al., 2006). The MSPD method is based on the homogenization of a viscous, solid or semi-solid sample with an abrasive solid support material in a glass mortar, in order to perform the complete disruption and dispersal of the sample. After blending, the sample is transferred into a column and analytes are eluted with appropriate solvent. Complete disruption of the sample and its dispersion over the support surface greatly enhance surface area for the sample extraction. Furthermore, interferences are retained on the adsorbent and in that way, extraction and clean-up are performed simultaneously, reducing the analysis time and the amount of solvent used (Barker, 2000; Kristenson et al., 2006).

Reversed-phase materials such as C8 and C18-bonded silica are the most commonly used adsorbents, because their lipophilic properties enable good disruption, dispersion and retention of lipophilic species (Lambropoulou & Albanis, 2007). Several methods based on use of these adsorbents have been used for determination of several pesticides classes including OPPs and OCPs in tomato, lettuce, orange, lemon, grapefruit, pear and plum (Torres et al., 1995), carbamates in orange, onion, grape and tomato (Fernández et al., 2000), eight fungicides in orange, apple, tomato, carrot and zucchini (Navarro et al., 2002), thirteen fungicides and insecticides in pepper, lettuce, tomato, orange, apple and pear (Torres et al.,



1997), five fungicides in orange, lemon, banana, pepper, chard and onion (Blasco et al., 2002), five pesticides in strawberry, orange, potato, pear and melon (Pous et al., 2001), five pesticides in onion (Rodrigues et al., 2010), and 14 pesticides in tomato, pepper, orange, raspberry, banana, cucumber, lemon, peach, grape, apple, grapefruit, pear, red currant and leek (Kruve et al., 2008). Besides C8 and C18-bonded silica, florisil has been successfully used for determination of OCPs in tomato juice (Albero et al., 2003), lemon, orange, apple, mango, grapes, banana, carrot, potato, onion, cucumber, tomato, cabbage, spinach and wheat (Abhilash i sar., 2007; 2009), pyrethroids in cucumber, eggplant, cabbage and peas (Ling & Huang, 1995), nine pesticides in artichoke, lettuce and tomato (Viana et al., 1996), phenthoate (Z-Y. Li et al., 2002), OCPs (Z. Shen et al., 2005; X. Shen et al., 2006) and five pesticides in soil (X. Shen et al., 2007). Also,  $\text{Al}_2\text{O}_3$  has been used as an adsorbent in determining of 15 pesticides in corn, potato and cabbage (Lin et al., 2010), while Bogialli et al. (2004) used sand for carbamates determination in lettuce, zucchini, spinach, tomato, apple and pear. Basically, the adsorbent choice depends on analyte polarity and interferences which could be co-extracted from sample matrix.

Also, the nature of the elution solvent is crucial for efficient pesticides elution from the adsorbent (Albero et al., 2003; Blasco et al., 2002; 2002a; Bogialli et al., 2004; Chu et al., 2005). The MSPD expansion in the last decade is evidenced not only by over 360 papers dealing with its applications, but also by reviews that have been published (Barker, 2000, 2000a, 2007; Bogialli & Di Corcia, 2007; Garc  a-L  pez et al., 2008; Kristenson et al., 2006; Moreda-Pi  ero et al., 2009). Compared with other extraction techniques, the MSPD performance was usually similar or superior, and results depending on the target analyte and sample matrix (Abhilash & N. Singh, 2009a; Gilbert-L  pez et al., 2010; Montes et al., 2009).

In comparison to traditional extraction methods, MSPD approach has several advantages, including simplified and faster sample-treatment, reduced use of toxic solvents, eliminated emulsion formation and increased selectivity and sensitivity. In MSPD, the sample extraction and clean-up are performed in the same step by use of small amounts of adsorbent and solvent, thus reducing the cost and analysis time. As a drawback, a number of applications still use large volumes of solvents for extraction and clean-up, which requires solvent evaporation. There is every reason to believe that solving of this problem will make MSPD more useful in the near future.

## 9. Conclusion

The sample extraction step, which accounts for about two-thirds of the total analysis time, is still the weakest link and the time-determining step in the whole analytical procedure. It is also the primary cause of errors and discrepancy between laboratories. However, in the recent past, improvements in the sample preparation techniques for different environmental samples have led to modification of the existing methods and development of new techniques, in order to save time and reduce use of chemicals and thus improve the overall performance of analytical process. As a result, several rapid, low cost, environmentally friendly, and readily automated methods of extraction are now available. Besides, because of the complexity of the matrices, extraction is usually followed by very specific clean-up procedures to achieve accurate sample quantification, so the new methods are modified in order to achieve a compromise between cost, selectivity, and sensitivity.

Reduced solvent methods, including supercritical fluid extraction (SFE), solid phase extraction (SPE), solid phase microextraction (SPME), microwave assisted extraction (MAE),



accelerated solvent extraction (ASE), QuEChERS and matrix solid phase dispersion (MSPD) have grown in their maturity, which increased application of these techniques in pesticide analysis of plant and soil matrices. Although the composition of environmental matrices such as plants and soil varies from place to place, which requires application of different approaches and strategies, the development of a uniform procedure is highly encouraged. Future developments in all areas of analytical sample preparation are expected to continue to be application-driven in a quest for improved recovery, higher sample throughput, and reduced consumption of organic solvent with capability to provide accurate results.

## 10. Acknowledgment

This study was carried out as part of the project No TR31043, supported by the Ministry of Science and Technological Development of the Republic of Serbia.

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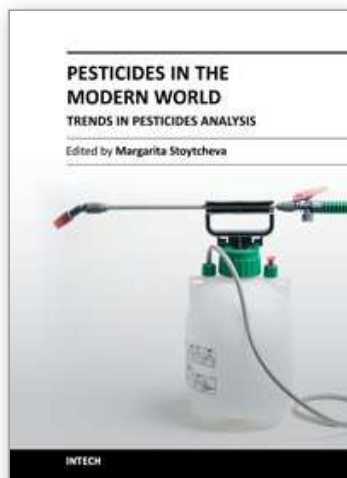
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## **Pesticides in the Modern World - Trends in Pesticides Analysis**

Edited by Dr. Margarita Stoytcheva

ISBN 978-953-307-437-5

Hard cover, 514 pages

**Publisher** InTech

**Published online** 21, October, 2011

**Published in print edition** October, 2011

The book offers a professional look on the recent achievements and emerging trends in pesticides analysis, including pesticides identification and characterization. The 20 chapters are organized in three sections. The first book section addresses issues associated with pesticides classification, pesticides properties and environmental risks, and pesticides safe management, and provides a general overview on the advanced chromatographic and sensors- and biosensors-based methods for pesticides determination. The second book section is specially devoted to the chromatographic pesticides quantification, including sample preparation. The basic principles of the modern extraction techniques, such as: accelerated solvent extraction, supercritical fluid extraction, microwave assisted extraction, solid phase extraction, solid phase microextraction, matrix solid phase dispersion extraction, cloud point extraction, and QuEChERS are comprehensively described and critically evaluated. The third book section describes some alternative analytical approaches to the conventional methods of pesticides determination. These include voltammetric techniques making use of electrochemical sensors and biosensors, and solid-phase spectrometry combined with flow-injection analysis applying flow-based optosensors.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Rada Đurović and Tijana Đorđević (2011). Modern Extraction Techniques for Pesticide Residues Determination in Plant and Soil Samples, *Pesticides in the Modern World - Trends in Pesticides Analysis*, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-437-5, InTech, Available from: <http://www.intechopen.com/books/pesticides-in-the-modern-world-trends-in-pesticides-analysis/modern-extraction-techniques-for-pesticide-residues-determination-in-plant-and-soil-samples>

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