Talanta 86 (2011) 8–22

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Review

Solventless and solvent-minimized sample preparation techniques for determining currently used pesticides in water samples: A review

Maciej Tankiewicz*, Jolanta Fenik, Marek Biziuk

Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, ul. G. Narutowicza 11/12, 80-233 Gdańsk, Poland

ARTICLE INFO

Article history:
Received 13 June 2011
Received in revised form 19 August 2011
Accepted 28 August 2011
Available online 1 September 2011

Keywords:
Pesticides
Environment
Solventless and solvent-minimized techniques
Sample preparation
Water samples

ABSTRACT

The intensification of agriculture means that increasing amounts of toxic organic and inorganic compounds are entering the environment. The pesticides generally applied nowadays are regarded as some of the most dangerous contaminants of the environment. Their presence in the environment, especially in water, is hazardous because they cause human beings to become more susceptible to disease. For these reasons, it is essential to monitor pesticide residues in the environment with the aid of all accessible analytical methods. The analysis of samples for the presence of pesticides is problematic, because of the laborious and time-consuming operations involved in preparing samples for analysis, which themselves may be a source of additional contaminations and errors. To date, it has been standard practice to use large quantities of organic solvents in the sample preparation process; but as these solvents are themselves hazardous, solventless and solvent-minimized techniques are coming into use. This paper discusses the most commonly used over the last 15 years sample preparation techniques for monitoring organophosphorus and organonitrogen pesticides residue in water samples. Furthermore, a significant trend in sample preparation, in accordance with the principles of 'Green Chemistry' is the simplification, miniaturization and automation of analytical techniques. In view of this aspect, several novel techniques are being developed in order to reduce the analysis step, increase the sample throughput and to improve the quality and the sensitivity of analytical methods. The paper describes extraction techniques requiring the use of solvents – liquid–liquid extraction (LLE) and its modifications, membrane extraction techniques, hollow fibre-protected two-phase solvent microextraction, liquid phase microextraction based on the solidification of a floating organic drop (LPME-SFO), solid-phase extraction (SPE) and single-drop microextraction (SDME) – as well as solvent-free techniques – solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE). The advantages and drawbacks of these techniques are also discussed, and some solutions to their limitations are proposed.

Contents

1. Introduction 9
2. Currently used pesticides 9
3. Techniques of isolating and/or preconcentrating pesticides from water samples 10
   3.1. Passive dosimetry 11
   3.2. Modification of liquid–liquid extraction 11
   3.3. Hollow fibre-protected two-phase solvent microextraction (HF(2)ME) 13
   3.4. Membrane extraction 14
   3.5. Liquid-phase microextraction based on the solidification of a floating organic drop (LPME-SFO) 14
   3.6. Single-drop microextraction (SDME) 14
   3.7. Solid-phase extraction (SPE) 15
   3.8. Solid phase microextraction (SPME) 16
   3.9. Stir bar sorptive extraction (SBSE) 17

* Corresponding author. Tel.: +48 58 347 21 10; fax: +48 58 347 26 94.
E-mail address: maciej.tankiewicz@gmail.com (M. Tankiewicz).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.08.056

4. Final determination 17
5. Conclusions 20
6. Acronyms 20
References 20

1. Introduction

Water is the source and support of life on Earth. It is essential for human health and well-being. Its deteriorating quality, however, has become a serious threat not just to the health and life of human beings, but also to the existence of flora and fauna. Desertification is affecting large areas of the Earth, and water, especially clean water, is a highly desirable and increasingly expensive asset. Moreover, the continuing increase in the human population means that the demand for drinking water is rising as well. Meanwhile, ever larger amounts of pollutants are entering the world's waters as a result of its intensive industrialization. This and the development of new technologies have involved the consumption of chemicals, including pesticides, on a vast scale. The latter are widely used to control all manner of agricultural production and to prevent the spread of diseases transmitted by insects and rodents [1–3]. The range of applications of pesticides is continually expanding, hence their consumption is ever increasing and more of them are getting into the environment [4,5].

The need to determine numerous contaminants present in the environment in trace amounts means that laboratories have to be capable of applying the relevant analytical procedures. Laboratories also have to be equipped with the necessary tools for obtaining reliable results, not to mention state-of-the-art apparatus enabling large numbers of compounds to be quickly and reliably determined in multifarious matrices [6,7].

One of the basic ways of limiting the adverse effects of pesticides on human health is monitoring of these compounds. In Poland, numerous monitoring studies are in progress, but there is still no regular monitoring of pesticide contents in waters. The numerous regulations that have come into force concerning permissible levels of pesticide residues [8–12], are driving the development of new analytical techniques and the improvement of existing ones. That is why attempts have been made to seek new solutions that would enable the largest possible number of compounds at low concentrations to be determined in small-volume samples.

2. Currently used pesticides

Nowadays, pesticides are applied not only in agriculture, but also in many spheres of life. Over 800 active ingredients are sold worldwide in tons of thousands of formulations [13]. The range of applications of pesticides is continually expanding, hence their consumption is ever increasing and more of them are getting into the environment. In 2009 sales of pesticides in Poland reached 49 760.8 tons, according to figures from the Ministry of Agriculture and Rural Development [14]. In the same year in Great Britain applied 20 249 tons of pesticides, according to data from the Food and Environment Research Agency [15]. It is estimated that EU countries consume more than 300 000 tons of pesticides per annum on crop protection alone. The world market for pesticides is estimated at $33.59 billion, of which the Unites States represents the largest part, in terms of dollars (33%) and pounds of active ingredients (22%) [16]. World pesticide amount used was approximately 5.2 billion pounds in both 2006 and 2007 [17]. In 2010 China pesticides sales amounted to 51.8 billion Yuan [18].

The rising trend in pesticide consumption is set to continue for many years to come, because the human population of the Earth is increasing and the demand for food is ever greater. Moreover, the urbanization of the world means that less land is given over to farming; the maximum yield from the smallest possible land area is thus the order of the day. Rising living standards mean that consumers want their food to be as fresh, tasty and good-looking as possible. Another problem is that pests develop resistance to pesticides that have been applied for a long time. Hence the never-ending search for new, more effective compounds that would combat larger groups of pests and yet be as innocuous as possible towards humans and animals, not to mention cheap. Figs. 1 and 2 show sales of pesticides in selected countries of the EU in 2006–2008 [19].

The trend at present is to find pesticides that act only in accordance with their intended action, and do not harm humans, or other flora and fauna. Unfortunately absolute selectivity is impossible to achieve in practice [2]. The factor determining whether a compound should be used or not, apart from its selectivity, is its rapid biodegradability, and this criterion applies not only to the pesticides themselves but also to their metabolic products. It goes without saying, of course, that pesticides should be environmentally as harmless as possible. After many years it was discovered that some pesticides, especially organochlorine pesticides (OCP), were toxic towards many more organisms than had at first been assumed. Thus, OCP began to be withdrawn and be replaced by compounds that are biodegraded quickly. However, in 2005 about 1% of all pesticides being applied were still OCP [2]. But although they are no longer applied, OCP are still present in the environment because of their considerable longevity (up to 30 years). They can also be transported at great distances by air and water. In place of OCP, organophosphorus and organonitrogen pesticides (OPP + ONP) began to be used. They have become very popular because they are cheap and readily available, have a wide range of efficacy, are able to combat a large number of pest species, and have a shorter environmental half-life than their organochlorine predecessors. One of the principal classes of compounds used for plant protection, organophosphorus pesticides (insecticides) embraces all organic compounds containing phosphorus atoms. Usually, they are in the form of esters and are degraded fairly easily, they are very poorly soluble in water, though better so in organic solvents and fats. It is estimated that OPPs are worth nearly 40% of the global market and that they are expected to maintain dominance for some time into the future [13].

The umbrella term 'organonitrogen pesticides' is a convenient way of referring to the large number of nitrogen-containing organic pesticides. In practice, however, these pesticides are known by the names of the various chemical classes. In the literature the term 'organonitrogen pesticides' usually refers to carbamates and triazines and their derivatives [3]. Carbamates (with OPP) are among the most important chemicals used for protection against agricultural and household pests.

Recently, after the decision of the US Environmental Protection Agency (EPA) about phase out certain uses of the organophosphate insecticides (e.g. chlorpyrifos) – due to their toxic effects on humans – the sales of insecticides containing pyrethroids have increased sharply [20]. Currently, pyrethroids are the most prevalent household insecticides for both indoor and outdoor applications, because of their selective insecticidal activity, non-persistence in the

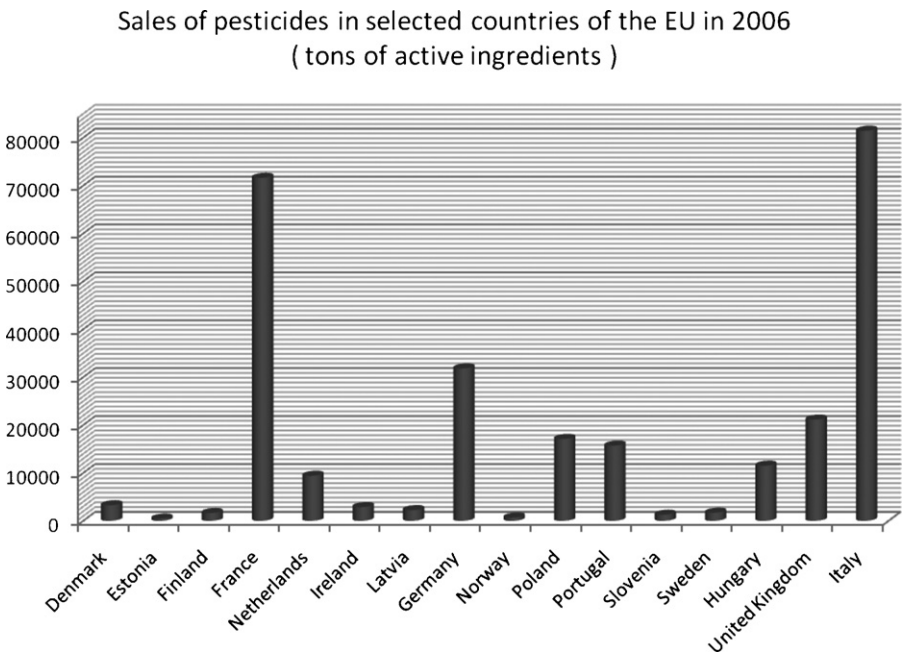

Fig. 1. Sales of pesticides in selected countries of the EU in 2006 [19].

environment and relatively lower mammalian toxicity than OPP [21]. According to EPA usage data, approximately 1000 tons of permethrin are applied annually to agricultural, residential and public health uses sites [22]. Nevertheless, the OPP + ONP are still the most popular pesticides and their usage is still growing, because their reliability, wide range of applications and prices. Therefore, this paper focuses on mainly these groups of compounds.

3. Techniques of isolating and/or preconcentrating pesticides from water samples

Monitoring pesticide residues in water is a matter of urgency. The choice of analytical methodology depends largely on the sample matrix (sample type) and the chemical structure of the target analytes. It also depends on EU and Health Ministers regulations regarding the maximum admissible level of a particular pesticide in water, which usually is 0.10 $\mu g\,L^{-1}$ [23]. The analytical procedure consists of numerous stages, the most important of which is the collection of a sample and its preparation for analysis. This stage is a complicated process, and its operations can be both a cause of analyte loss and a source of additional contamination. At this stage all errors will affect on the final result of determination. A further difficulty is the fact that the collection and sample preparation step take up to *ca* 2/3 of the time required to perform the complete analysis. Also in the sample preparation process large quantities of organic solvents are used and because they are toxic themselves pose a threat to the environment. This is why chemists are now striving to develop environmentally friendly analytical methodologies that

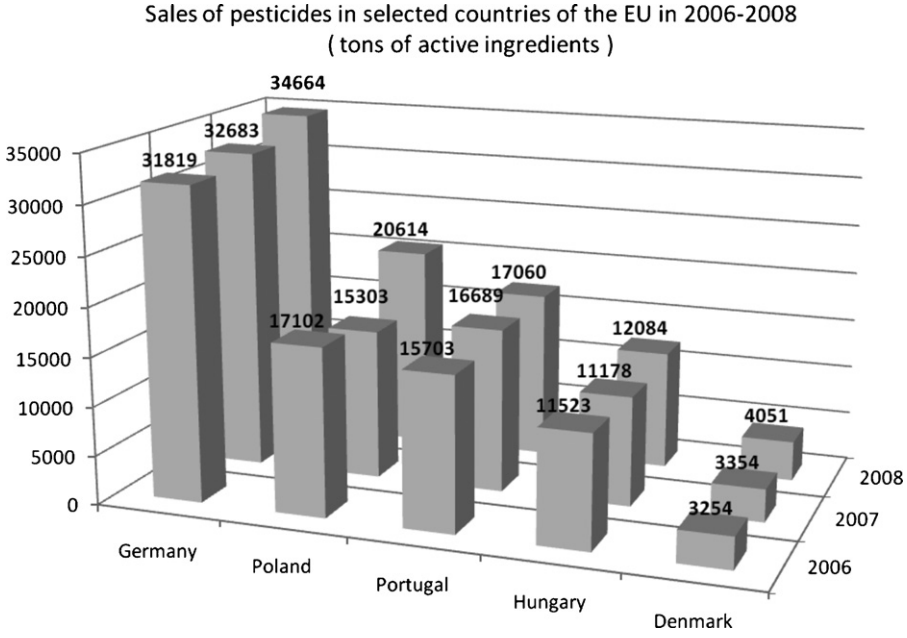

Fig. 2. Sales of pesticides in selected countries of the EU in 2006–2008 [19].

are consistent with the principles of 'Green Chemistry'. This ensures that:

- the use of chemical reagents, particularly organic solvents, is eliminated or at least substantially reduced,
- the application of highly toxic reagents is eliminated,
- the labour- and energy consumption of processes is reduced,
- a broad spectrum of target analytes can be determined in a single analytical run [24–26].

The rapid development of new techniques in analytical chemistry (miniaturization, automation) has meant that the consumption of solvents in the analysis of pesticide residues would be very substantially reduced; very often the use of solvents would be eliminated at all if solvent-free techniques were applied [27]. Proceeding in this direction we can see how extraction techniques have evolved from the classical liquid–liquid extraction (LLE), through liquid-phase microextraction (LPME), solid-phase extraction (SPE) to solvent-free techniques like stir bar sorptive extraction (SBSE) or solid phase microextraction (SPME). The main advantages of these techniques are minimalization of consumption harmful solvents, and typically, the high enrichment factor. The improved sensitivity makes it possible to minimize the amount of sample needed for the analysis. Ideally, sample preparation stage should be as simple as it possible, because it not only reduces the time required, but also decreases the possibility of introducing contaminants. Fig. 3 presents trends in the development of techniques of sample preparation.

Automation of analytical techniques can reduce labour- and energy consumption in analytical procedures, as well as it eliminates the human factor. Most of the activities (both in the field and in the laboratory) related to sample preparation is performed manually. All operations, including sampling and sample preparation, are performed using a suitable apparatus. The monitoring studies use devices that must exhibit the following characteristics: ability to obtain information with little or no time delay, the possibility of carrying out measurements on a continuous and long period of so-called autonomous work. At present it is common to combine sample preparation technique with chromatographic analysis (either *off-line*, *at-line* or sometimes even *on-line*) e.g. GC with SPE *on-line* [28] and apply multi-residue methods [29–32]. The *off-line* procedures can be good alternative when the number of samples is small, because usually there is no need for an automated method and the time-consuming development of such a method. Conventional methods will suffice. Setting up an automated method, either *at-line* or *on-line*, becomes more worthwhile when the number of analysed samples increases. The automation typically improves the quality of the data, increases the sample throughput, decreases costs and improves the productivity of personnel and instruments. The *on-line* systems are beneficial when the analytes are labile, amount of sample is limited, or very high sensitivity is required [33].

The selection of an extraction technique is made on the basis of several factors. Obviously, the sample preparation must be tailored to the final analysis. The sample matrix and the type and amount of analytes in the sample are of primary importance. Also crucial are speed of extraction, complexity of the instrumentation, simplicity and flexibility of the method development, and ruggedness of the method. Moreover, a method good for target-compound analysis may not be good for comprehensive chemical profiling of samples. Selectivity of the sample preparation stage is often a key factor for target-compound analysis while an exhaustive extraction is the better choice for profiling.

From analytical point of view, environmental samples are highly diverse and complex: the factors affecting the nature of the sample are the sampling site, the type of matrix, the presence of interferents and the low concentration of target analytes. Whether or not the analysis yields reliable information about the sample content depends to large extent on the proper sample preparation. The quality of sampling and sample pretreatment largely determines the success of an analysis from complex matrices. For analysis representative samples are required, and these are collected using appropriate samplers. Water samples are usually collected with a scoop and poured into a dark glass bottle without a concave bottom, then transported to the laboratory and stored at 4 °C without light. In the case of tap water characterized a relatively simple matrix, the removal of solid contaminants present in samples can be omitted, surface water samples require proper preparation before analysis. The most of water samples have to be filtrated. In the case of more complex sample matrix, it should be preserved by adding bacteriocides [3,34].

3.1. Passive dosimetry

Passive dosimetry is applied at the sample collection stage, with which analytes can be isolated and preconcentrated at the same time. The free transport of mass takes place across a membrane to the sorbent as a consequence of the difference in chemical potentials of the compounds in the sorbent and the water in which the sampler has been immersed [35]. For sampling pesticides from coastal waters and rivers one uses polyethylene dosimeters packed with iso-octane or stainless steel dosimeters filled with cyclohexane as sorbent. Three or four samplers of one type are deployed, usually for 30 days. Most passive samplers are fairly small in size, which substantially reduces the amounts of organic solvents required (the volume of the dosimeter chamber is *ca* 1 mL), makes them easy to transport and to assemble at the deployment site. With the use of passive dosimeters there are fewer steps in the analytical procedure, which means results are more reliable and reproducible. The shortcomings of such dosimeters, however, include an insufficient sensitivity to short fluctuations of target analyte levels and a susceptibility to environmental factors like temperature and water movement, which means that samplers have to be calibrated in order to set the rate of analytes collection. Table 1 characterizes some of the passive dosimeters used to sample pesticides from water [35–37].

3.2. Modification of liquid–liquid extraction

Currently the subject literature focuses mainly on the techniques for the isolation, preconcentration and final determination of analytes, all of which can affect the reliability of the information obtained about a sample. This is due to the low concentrations of analytes and the complexity of matrices, the constituents of which may be a source of interferents and errors in later stages of the analysis.

Because of the low concentrations of pesticides in the aquatic environment, it is essential not just to isolate these organic compounds from the complex matrix but also to preconcentrate them prior to their final determination: extraction and/or preconcentration raises the concentrations of target analytes to a level enabling their determination. Analytes are also transferred from the primary matrix to a secondary one with the concomitant elimination of interferents. The choice of technique depends on the properties of the target analytes: their volatility, polarity, stability, solubility in water and organic solvents. One of the oldest extraction techniques and in the same time one of the most common is liquid–liquid extraction (LLE). The solvents in LLE are usually dichloromethane [38–41], mixtures of petroleum ether and dichloromethane [42] or hexane and dichloromethane [39]. Though fairly simple and cheap, this technique has a number of drawbacks: it requires relatively large quantities of toxic solvents, there is a risk of emulsions

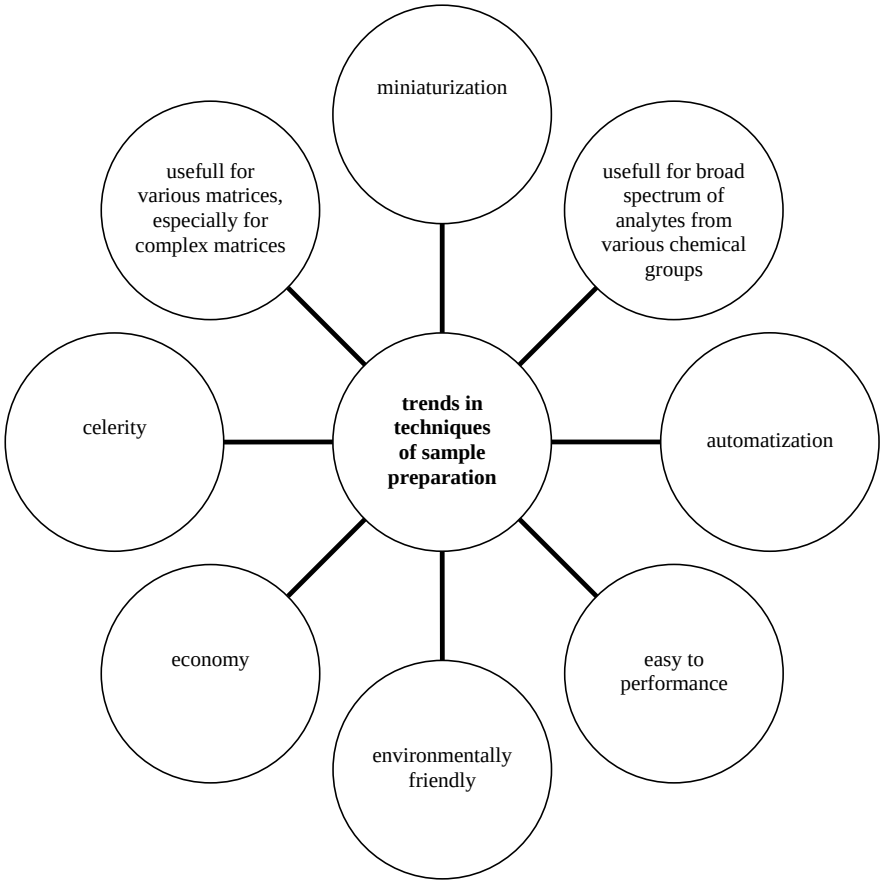

Fig. 3. Trends in the development of techniques of sample preparation.

forming during stirring, and there is the problem of disposal of the post-extraction solvents. To achieve the desired preconcentration coefficient, the excess solvent usually has to be evaporated. Also extract cleanup is often necessary. To minimize their disadvantages numerous improvements have been made to this method, most of which have involved miniaturizing the process to reduce the amounts of solvents consumed. One of the example is micro liquid–liquid extraction (MLLE), which is easy, fast and use only few microlitres of solvents. The appropriate construction and miniaturization of the extraction vessel make it possible to use small amounts of solvent that are small in relation to the quantities of sample extracted (*ca* 1 mL of solvent per 1 L of sample). The typical solvents used for microextraction are: dichloromethane, toluene and methyl-tert-butyl ether [43,44]. Zapf et al. [44] applied MLLE coupled with GC–ECD and GC–NPD to determine 82 OPP, triazines and acetanilide pesticides in drinking water. The limits of detection (LODs) were below 100 ng L^{-1} and relative standard deviations (RSD) were in the range of 5.2–7.9%. For extraction of 400 mL water sample, 500 μL of solvent (toluene) was used. This technique is rapid, simple and eliminates the need to cleanup of the extract.

The dispersive liquid–liquid microextraction has emerged as a next attractive alternative for traditional LLE, because it is fast, inexpensive, easy to operate, consumes low volume of organic solvent and provides high enrichment factors [43–45]. A scattering solvent, e.g. acetone or methanol (0.5–2 mL) with addition of extraction

Table 1
Parameters characterizing some of the passive dosimeters used to sample pesticides from water [35–37].

Sampler	Full name	Description of construction	Analytes sampled	Typical sampler exposure time
Passive dosimeter for sampling organic compounds from water	–	Housing: acid-resistant steel, sorbent: organic solvent, membrane: variable – selected according to target analytes	Acidic herbicides and triazines	1 month
POCIS	Polar organic chemical integrative sampler	Housing: two rings of stainless steel, sorbent: depends on the analyte to be preconcentrated; usual beds: Isolute ENV+, Ambersorb 1500, S-X3 Bio-Beads, membrane: polyethersulfone (47 mm diameter, 0.1 μm pore size)	Herbicides/polar pesticides	Up to 2 months
TRIMPS	Trimethylpentane-containing passive sampler	Sorbent: 2,2,4 trimethylpentane, membrane: low-density polyethylene	Pesticides of various classes	1 month
MESCO	Membrane-enclosed sorptive coating	The sampler consists of a hydrophobic solid receiving phase (polydimethylsiloxane) enclosed in a water filled hydrophilic semi preamble membrane	Pesticides of various classes	Up to 1 month

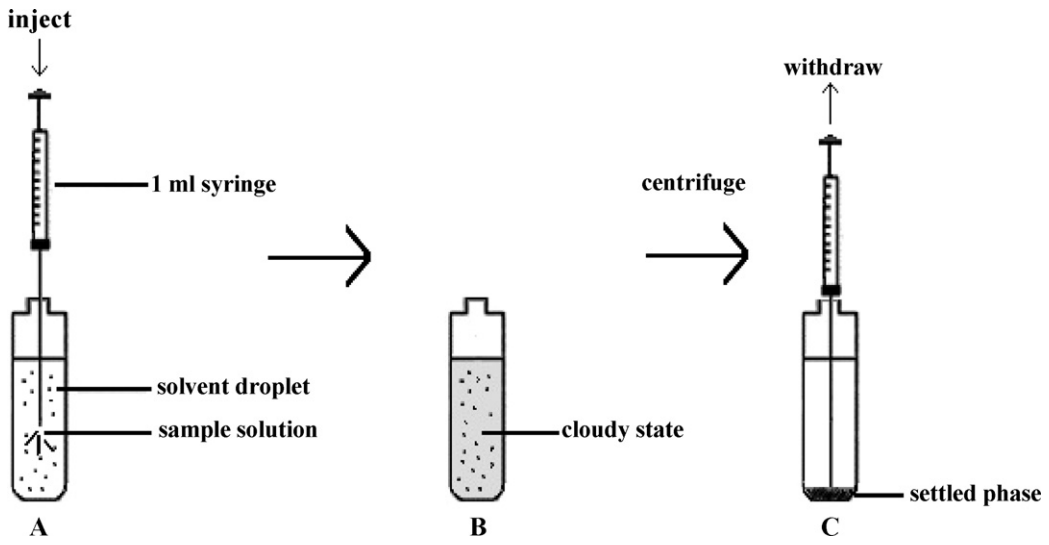

Fig. 4. Dispersive liquid–liquid microextraction procedure [45].

solvent, e.g. CCl_4, CS_2 (10–50 μL), is added to the water sample (5–10 mL) (A). This produces a turbid solution (B), which is then centrifuged to obtain *ca* 5 mL extract phase (C) [43,45–49]. Fig. 4 illustrates the dispersive liquid–liquid microextraction procedure [45].

By reduction the amounts of solvents used, some of the inconveniences limiting the technique's application in the liquid–liquid system are eliminated. The DLLME technique can be coupled with GC and HPLC [50]. Assadi et al. [47] applied DLLME coupled with GC–FPD to determine 13 OPP in river water, well water and farm water. For extraction of 5 mL water sample, 12 μL of extraction solvent (chlorobenzene) and 1 mL of disperser solvent (acetone) were used. The LODs were in the range of 3–10 pg mL^{-1} and RSD were 1.2–5.6%. Recently, Zhao et al. [51] applied sequential isolation of analytes (solid-phase extraction (SPE) combinated with DLLME) coupled with GC–MS to determine amide herbicides in tap water and reservoir water. Analytes were adsorbed from 100 mL of water sample onto a sorbent (multiwalled carbon nanotubes – MWCNTs, 100 mg) and next they were eluted with 1 mL of acetone. After elution, the DLLME technique was performed and then extract was analysed. For DLLME of 5 mL water sample, 25 μL of carbon tetrachloride (CCl_4) (extraction solvent) was used. The LODs were in the range of 0.002–0.006 μg L^{-1} and RSD were 2.6–8.7%. The non-selective characteristic of the extraction solvents can be sometimes a disadvantage of DLLME. To overcome this difficulty and to eliminate the use of dispersive solvents making the technique more environmental friendly, new alternatives are being developed like the use of ionic liquids (IL-DLLME) and ultrasonic radiation. Recently, He et al. [52] used ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$) as extraction solvent for the determination of 4 OPP in tap water, well water, rain and river water samples. The LODs were in the range of 0.1–5.0 μg L^{-1} and RSD were 1.7–4.5%. Ionic liquids belong to non-molecular solvents with unique properties such as negligible vapour pressure associated to a high thermal stability. Hydrophobic ionic liquids incorporating the imidazolium cation and hexafluorophosphate anion have higher density than water. After comparing them with commonly used solvents they are more compatible with reversed-phase HPLC due to the non-harmfulness to column [53–56]. Due to its simplicity and low extraction time, DLLME is becoming an attractive preconcentration technique in determination of pesticides water analysis in water samples [49,50,57].

In order to improve the extraction efficiency of polar pesticides by choosing a dispersive solvent that can be partitioned in the extractant droplets, Fuh et al. [58] developed partitioned dispersive liquid–liquid microextraction (PDLLME) combined with HPLC–UV for the determination of 8 phenylurea herbicides in river water samples. The polar compounds were extracted into the dispersed dichloromethane (60 μL) droplets containing tetrahydrofuran (1000 μL). Under the optimized conditions, the LODs were in the range of 0.1–0.28 ng mL^{-1} and RSD were 1.5–5.9%.

Vortex-assisted liquid–liquid microextraction (VALLME) is an example of resolving DLLME drawbacks whereby dispersion of the extractant phase into the aqueous is achieved for the first time using vortex mixing, a mild emulsification procedure [59]. The fine droplets could rapidly extract target analytes because of the shorter diffusion distance and larger interfacial area. This extraction technique has been efficiently applied by Jia et al. [60] in the analysis of 1 OPP and 5 pyrethroids by GC–μECD in tap water and snow water samples. For extraction of analytes from 25 mL water sample, 30 μL of toluene was used. The LODs were in the range of 3.2–10 ng L^{-1} and RSD were 3.8–11.3%. This microextraction technique has the advantages such as easy operation, shorter extraction time than DLLME and can be used in the pesticides multiresidue analysis.

3.3. Hollow fibre-protected two-phase solvent microextraction (HF(2)ME)

HF(2)ME is often referred to in the literature as liquid-phase microextraction (LPME), what is confusing, since the same designation is also used for single-drop microextraction (SDME). Above all, only a tiny amounts of few microlitres of organic solvent is required, application of organic solvent also eliminates necessity of extract cleanup prior to qualitative and quantitative determinations. The method is straightforward, quick and inexpensive. It is based on the partition of analytes between the aqueous solution and the small quantity of organic solvent in a microporous tube (the rod configuration). The hollow fibre can be also in the U-shape configuration. Around 2–3 μL of solvent are drawn into a microsyringe (10 μL) – for the extraction of OPP + ONP this is usually toluene, hexane or 1-octanol. Then to the microsyringe needle is connected to a polypropylene microporous tube (a hollow fibre) *ca* 1.3 cm in length, which is coated with a thin film of polymer (internal diameter 0.6 mm; wall thickness 0.2 mm; pore diameter 0.2 μm). The membrane protects the solvent from

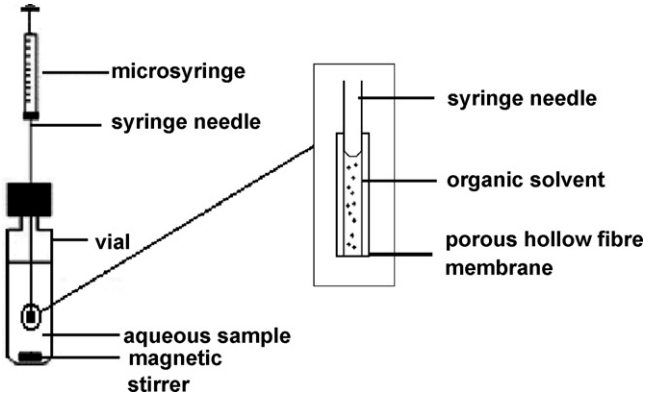

Fig. 5. The hollow fibre-protected two-phase solvent microextraction setup [43].

particulate matter or soluble polymeric material (proteins) present in the sample. The solvent is introduced to the microporous tube and then transferred to a 4 mL vial containing the aqueous solution. The process is assisted by stirring (600–1000 rpm). On completion of the extraction, *ca* 1–1.5 μL is again taken up by the microsyringe, after which the analysis is performed using chromatographic techniques, usually: GC–MS, GC–FTD [43,61,62]. Fig. 5 illustrates the hollow fibre-protected two-phase solvent microextraction setup [43].

Huang and Chen [62] applied HF(2)ME coupled with GC–MS to determine 4 OPP in lake water sample. For extraction of 20 mL water sample, 3.5 μL of cyclohexane was used. The LODs were in the range of 0.006–0.2 μg L^{-1} and RSD were 3.5–8%. The disadvantage of this technique is the relatively long extraction time of 20–60 min compared to single-drop microextraction (SDME), which takes only 5–20 min. In addition, only part of the extract is analysed, and the fibre has to be properly prepared prior to extraction [27,43]. For more complex matrices and moderately polar pesticides Basheer et al. [63] developed binary solvent based on HF(2)ME coupled with GC–MS to determine 6 OPP in wastewater samples. The mixture (1:1) toluene: hexane was used as solvent. The LODs were in the range of 0.3–11.4 ng L^{-1} and RSD were 9–13%. This technique gave higher analytes enrichment, especially when it was applied to complex matrices (wastewater).

3.4. Membrane extraction

Membrane extraction can replace traditional LLE as it requires the use of smaller amounts of solvent or even none at all. This eliminates a number of disadvantages, among them the problem of emulsion formation. Table 2 compares membrane extraction techniques used for determining OPP + ONP in water samples [64].

Membrane-assisted solvent extraction (MASE) was used by Hauser et al. [65] for the extraction of 7 triazines from river water samples in combination with large volume injection gas chromatography mass spectrometric detection (GC–MS). The membrane (nonporous polypropylene) consisted of tubing with an internal diameter of 6 mm, which was filled with 500 μL hexane. The LODs were in the range of 1–10 ng L^{-1} and RSD were 2.1–14.3%. The same research group developed a multiresidue method for the analysis of 64 pesticides (including 9 OPP and 7 triazines) extracted with 1 mL of cyclohexane. The LODs were in the range of 2–10 ng L^{-1} and RSD were 7–15%. Dimethoate was an exception with a RSD of 24% and LOD 50 ng L^{-1} [66]. The application of MASE to more polar compounds is limited due to the non-polar character of the membranes. Another disadvantage is time of extractions which is higher when compared to other commonly used techniques.

Table 2
Membrane extraction techniques used for determining organophosphorus and nitrogen pesticides in water samples [64].

Name of technique	Type of membrane	Phase combination donor/membrane/acceptor
Polymer membrane extraction (PME), membrane-assisted solvent extraction (MASE)	Non-porous	Water/polymer/water, organic/polymer/water, water/polymer/organic
Membrane micro liquid–liquid extraction (MMLLE)	Non-porous (microporous)	Water/organic/organic, organic/organic/water

Another membrane technique for the extraction of pesticides in water matrices is microporous membrane liquid–liquid extraction (MMLLE). Advantages of this technique compared to LLE are small sample volumes, the lack of emulsion formation, the clean extracts obtained and it can be coupled online to gas chromatography. Lüthje et al. [67] developed online microporous membrane liquid–liquid extraction-gas chromatography method (MMLLE–GC/MS) for the analysis of 8 ONP and 1 OPP in river water, lake water and sea water samples. The LODs were in the range of 1.6–15 ng L^{-1} and RSD were 4.2–25.6%. The flat-sheet membrane (porous polypropylene) consisted of two blocks, was used as a barrier between two phases: acceptor (toluene) and the aqueous donor solution (sample). The donor solution was pumped to the donor channel of the membrane block, while the acceptor was stagnant during the extraction period. Following the extraction, the extract was eluted to a sample loop in a large-volume GC injection valve and injected online into the gas chromatograph. MMLLE was also applied by Zhou et al. [68] to conduct the enrichment of 5 sulfonylurea herbicides in reservoir water, tap water and wastewater samples prior to non-aqueous capillary electrophoresis determination. The LOD was 0.4 ng mL^{-1} and RSD was 11%.

3.5. Liquid-phase microextraction based on the solidification of a floating organic drop (LPME-SFO)

LPME-SFO is another technique used for the sample preparation, introduced by Khalili-Zanjani et al. [69,70]. This technique involves placing 10 μL of a solvent, usually 1-undecanol [43,69], with the aid of a syringe on the surface of an aqueous solution contained in a 21 mL vial. The solvent must be insoluble in water, stable during extraction, poorly volatile and have a melting point close to room temperature (10–30 °C). The extraction is carried out in a water bath and assisted by stirring (*ca* 1250 rpm), which means that droplets of solvent appear on the surface of the solution. The vial containing the sample is then cooled in an ice bath, where the extraction solvent solidifies. After app. 5 min, the solid solvent is transferred to another vial and quickly melted. Finally, 2 μL of the extract are collected for chromatographic analysis. Khalili-Zanjani et al. [69] applied this technique with GC–FPD to determine 9 OPP in various water samples. The LODs were in the range of 0.01–0.04 μg L^{-1} and RSD were 3.5–8.9%. The technique is cheap, quick, sensitive and requires only small amounts of organic solvent. On the other hand, LPME-SFO involves several steps, which makes it laborious. The second big disadvantage is that the rate of extraction is slightly slow.

3.6. Single-drop microextraction (SDME)

SDME is a simple and inexpensive method of preparing samples. The extraction phase is a drop of organic solvent, so it is practically a solvent-free method. Analyte isolation and preconcentration take place in a single step. This technique is applicable to liquid, gaseous and solid samples. Despite these advantages, also

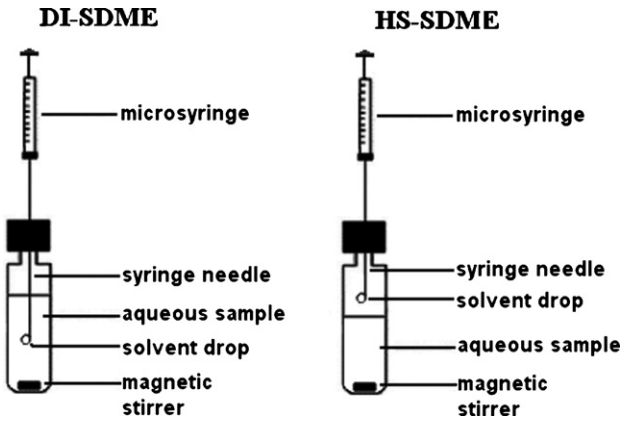

Fig. 6. The single-drop microextraction setup.

some disadvantages have been noticed and include: the difficulty of achieving a stable organic drop, air bubble formation, extraction is time-consuming and equilibrium can only be attained after a long time in most cases. SDME can be carried out in two different ways:

- direct immersion (DI) – makes use of the ability of a microdroplet of organic solvent to be retained at the tip of syringe needle immersed in the sample to be analysed; organic contaminants are then transferred from the aqueous (water matrix) to the organic phase;
- from the headspace (HS) – when solvent has been drawn into the syringe, the needle penetrates the membrane of the vessel containing the sample; in order to form a droplet, the syringe is fixed in such a way that the needle tip with the solvent drop is situated in accordance with the requirements of headspace analysis.

When the extraction is complete, the microdroplet is drawn back into the syringe needle and injected into a gas chromatograph (GC) or high-performance liquid chromatograph (HPLC) for further analysis.

Single-drop microextraction is easy to be applied. In comparison with traditional LLE, the ratio of solvent to water sample is very small. The universality of SDME makes it widely applicable to the analysis of pesticides in samples with a complex composition containing target analytes in trace amounts. If microextraction from aqueous samples gives good recoveries, then the type of extractant, the drop volume, the extraction time and the necessity of the stirring must be assessed and optimized. The choice of a suitable solvent (e.g. *n*-hexane, toluene, buthyl acetate) [71–74] ensures good sensitivity, precision and selectivity of the target compounds. Solvents choice should be based on a comparison of extraction selectivity and its yield. It is also important to take care of solvent drop losing during faster stirring and a long extraction time. Magnetic stirring accelerates extraction and shortens the time needed for thermodynamic equilibrium between the aqueous and gaseous phases to be reached. The stirring time (10–40 min) and speed (400–1300 rpm) must be selected so that the solvent drop does not become detached from the needle or dissolve in the aqueous phase. In SDME the amount of analyte extracted to the drop of organic solvent is strictly related to its volume. Drop volumes are usually in the 0.9–1.5 mL range. Analyte preconcentration is better and extraction is more efficient with larger drops. It should be remembered that injecting larger drop into the chromatographic system may cause band broadening in capillary GC. Moreover, drops larger than 2 μL are less stable and the reproducibility of results with such drops is poorer [71,72]. Fig. 6 shows the single-drop microextraction setup.

Xiao et al. [71] applied SDME with GC–FPD to determine 6 OPP in lake water sample. The LODs were in the range of 0.21–0.56 ng L^{-1} and RSD were 1.7–10%. Nowadays, both modes have been successfully used for the extraction of OPP + ONP in water samples [71–74]. Recently Liu and Lee [75] developed a new SDME procedure, which was termed continuous-flow microextraction (CFME). The drop of extraction solvent (1–5 μL) is injected by microsyringe into a glass chamber (0.5 mL) and held at the outlet tip of a polyetheretherketone (PEEK) connecting tube. The sample solution flows past the tube and through the glass extraction unit to waste. Extraction takes place continuously between the organic drop and the flowing sample solution. Because the drop of solvent makes full contact with the sample solution, the technique achieves higher concentration factor than static mode. He and Lee [76] applied CFME technique combined with HPLC–UV to determine 5 pesticides from different classes (simazine, fensulfothion, etridiazole, mepronil and bensulide) in reservoir water samples. The LODs were in the range of 0.6–4.0 ng mL^{-1} and RSD were 2.2–16.9%. CFME is demonstrated as a fast and sensitive single solvent drop microextraction technique, although more efforts are desired to improve the method precision and further simplify the procedure to enable it being automated to some degree.

3.7. Solid-phase extraction (SPE)

Solid-phase extraction (SPE) is one of the most widely used sample preparation technique in environmental analysis. The basic principle of SPE is sorption of analytes from an aqueous phase onto a sorbent. Analytes are eluted with appropriate organic solvents and then analysed by GC or HPLC. Compared to traditional LLE, SPE is simpler, requires lower volume of organic solvent, more convenient and easier to automate. There is no necessary evaporate off the solvent in order to achieve the desired enrichment factor of analytes. SPE sorbents are usually divided into three groups: chemically bonded silica, carbon materials and porous polymeric materials. Most of the sorbents in routine use take the form of extraction discs or columns. In the case of OPP + ONP, sorbents (silica gel, aluminium oxide, Florisil, porous polymers: XAD-2, XAD-4, XAD-7, XAD-16) usually modified with octadecyl groups were used [39,77–89]. The following solvents are routinely used to elute adsorbed analytes: methanol [79,82,83,85,90], ethyl acetate [28,39], dichloromethane [77,78,80,88], and mixtures of: methanol and water [84,87,89], methanol and acetonitrile [31,81], acetonitrile and water [86]. However, the conventional sorbents such as C_{18} silica, graphitized carbon black and macroporous polystyrene divinylbenzene (PS-DVB), show low retention for polar compounds [91,92]. In order to improve the SPE efficiency for polar compounds, many new hydrophilic sorbents and modified adsorbents through introducing the polar groups have been developed. The researches are going mainly in this direction.

Carbon nanotubes (CNTs) are example of carbonaceous nanomaterial and can be described as a graphite sheet rolled up into a nanoscale-tube. They have received a significant attention as a novel adsorbents for SPE and SPME, because of their high adsorption capacity, good thermal stability and wide pH range of application. There are two types of CNTs: single-walled (SWCNTs) and multiwalled (MWCNTs) nanotubes. SWCNTs have diameters between 1 and 10 nm and normally capped at the ends. In contrast, MWCNT diameters are much larger from 5 nm to a few hundred nanometers [93]. The applications of CNTs as SPE sorbents for extraction of pesticides from environmental waters have been reported many times in the literature [94–102]. For example, Katsumata et al. [95] applied MWCNTs as an adsorbent for the extraction of OPP (diazinon) from tap water samples. Next, the analyte was desorbed in acetonitrile and analysed using HPLC–UV. Under the optimized extraction conditions, the LOD was 0.06 ng mL^{-1} and RSD were in the range of 2.3–3.3%. Al-Degs et al. [96] applied solid-phase extraction with multivariate calibration

for simultaneous determination of three toxic pesticides (atrazine, methidathion and propoxur) in tap water and reservoir water samples without chromatographic separation. MWCNTs were used as adsorbent for pesticides preconcentration prior to multivariate analysis. The LODs were in the range of 2–3 $\mu g\,L^{-1}$ and RSD were 1–3%. Nevertheless, most of the reported work has focused mainly on the application of MWCNTs, and the target chemicals were limited to low polar compounds. SWCNTs have a much higher specific area and thus a stronger retention ability for polar compounds than MWCNTs. Li et al. [103] proposed oxidized SWCNTs and MWCNTs (OSWCNTs and OMWCNTs) to use as SPE sorbents to enrich polar OPP. The oxidation process with air introduced polar functional groups onto the surface of CNTs and significantly improved their adsorption ability. They applied SWCNTs, MWCNTs, oxidized SWCNTs and commercial Oasis HLB cartridge to isolate 6 OPP from seawater and reservoir water. The extract was analysed by GC–FPD. The LODs were in the range of 0.07–0.12 $\mu g\,L^{-1}$ and RSD were less than 10%. The results showed that OSWCNTs had a higher extraction efficiency than Oasis HLB for the extraction of methamidophos and about the same for the other four OPP.

Su et al. [104] applied molecularly imprinted polymer (MIP) for the cleanup and preconcentration of 4 OPP from complex matrix. The MIP was synthesized using monocrotophos as the template molecule, methacrylic acid as a functional monomer and ethylene glycol dimethacrylate as a cross-linker. After polymerization, MISPE was used for the selective preconcentration of four polar OPP from environmental samples (river water and tap water) prior to chromatography analysis (GC–NPD). The LODs were in the range of 10–32 $ng\,L^{-1}$ and RSD were 2.3–5.5%. The newly developed MISPE proved to be a powerful tool for the selective enrichment of polar pesticides. Its low cost of preparation and favorable compatibility with organic solvents allowed reliable, accurate analysis of the analytes within complex matrix at trace level.

3.8. Solid phase microextraction (SPME)

Solid phase microextraction (SPME) does not require the use of organic solvents. It is quick, universal, sensitive and convenient for use in the field and is simply applied in sample preparation. However the fibre is comparatively expensive, fragile and has limited lifetime. The idea of SPME is that analytes are adsorbed on a fibre coated with a suitable stationary phase, expressed from a microsyringe. The sensitivity of this technique depends primarily on the partition coefficient between the sample and the fibre stationary phase. Hence, the efficacy of preconcentration depends principally on the type of stationary phase and its thickness. But other parameters of the process are also important: sample volume and temperature, fibre exposure time, extraction vial volume and sample stirring.

The materials used for coating fibres include:

- polydimethylsiloxane (PDMS) [105–110],
- polyacrylate (PA) [106–109,111,112],

and also mixtures of:

- polydimethylsiloxane and polydivinylbenzene (PDMS–DVB) [105–107,112–116],
- carbowax and polydivinylbenzene (CW–DVB) [105,109,116],
- carbowax and molecularly imprinted resin (CW–TPR) [112].

One of the weakest aspects of SPME is that the commercially available fibres cover only the scale of polarity, which cause the lack of selectivity of the extraction process. Thus, recent years have seen an increase in interest in the preparation of tailor-made fibres with the aim of providing certain selectivity to the extraction process [117]. Recently Guan et al. [118] introduced a new sol–gel method for the preparation of SPME fibre, in which polydimethylsiloxane (PDMS) containing 3% vinyl group was physically incorporated into the silica sol–gel network, and then the extraction phase was partly cross-linked at 320 °C, so it could withstand 290 °C desorption temperature. This technique with GC–TSD was applied to determine 11 OPP in water samples and LODs were in the range of 0.39–19.9 $ng\,L^{-1}$ and RSD were 1.0–27.2%. Lee et al. [119] prepared amphiphilic and hydrophilic oligomers coated-SPME fibres using a sol–gel procedure. The fibres were stable up to 280 °C. This technique with GC–MS was applied to determine 6 triazines and LODs were in the range of 0.001–0.005 $\mu g\,L^{-1}$ and RSD were 6.7–10.3%.

Table 3
Comparison of SPME and SDME.

Parameters compared	SPME	SDME
Sensitivity and precision	Better	Worse
Sample transfer	Yes	No
Addition manual operation during analysis	No	Yes
Apparatus with a limited lifetime	Yes	No
High cost and specialist apparatus	Yes	No

Molecularly imprinted polymers (MIPs) have proven to be useful materials for SPME fibres. MIPs are cross-linked synthetic polymers obtained by copolymerizing a monomer with a cross-linker in the presence of a template molecule (print molecule). The polymer, with its template being washed away, contains recognition sites that are complementary in size, shape and chemical functionality to the template molecules. The produced imprinted polymer is able to rebind selectively with the template (analyte) and its analogous structures [120]. MIP is usually synthesized for a specific analytical purpose that implies the choice of a given template molecule. The structure and the functionalities of this molecule define the subsequent properties of the binding sites [121]. Djozan et al. [122] introduced a fast and straightforward method to prepare a monolithic and water compatible SPME fibre based on ametryn-imprinted polymer. The prepared fibre was used for extraction of 7 triazines from tap water samples. The MIP-SPME was coupled with GC–MS and LODs were in the range of 14–95 $ng\,mL^{-1}$ and RSD were 4.87–10.6%. The same research group [123] proposed MIP-SPME fibre produced by copolymerization of methacrylic acid–ethylene glycol dimethacrylate imprinted with atrazine, which was coupled with GC–MS, for extraction and analysis of triazines in tap water samples. The LODs were in the range of 20–90 $ng\,mL^{-1}$ and RSD were 4.15–9.69%. The combination of molecular imprinting and SPME would ideally provide a powerful analytical tool in terms of technology, simplicity, flexibility and selectivity characteristics.

Depending on where the fibre is situated in relation to the sample, SPME can be divided into Direct Immersion (DI-SPME) and Headspace (HS-SPME) types. Adsorbed analytes are usually transferred to the injection port of a gas chromatograph, where their thermal desorption and subsequent determination takes place. The advantage of this method is that the limited capacity of the adsorbent precludes column overloading. The method is difficult to optimize, however, and selectivity is poor in the case of analytes extracted from samples with a complex matrix composition.

Both SPME and SDME are alternatives to traditional extraction methods. Their superiority over classical LLE emerges from their rapidity, their consumption of minimal amounts of organic solvent and the possibility of determining compounds present in low concentrations. Table 3 compares SPME with SDME.

Recently Hu et al. [124] developed a novel liquid–liquid–solid microextraction (LLSME), which is the combination of solid-phase microextraction with liquid-phase microextraction. LLSME is based on porous membrane-protected molecular imprinted polymer

(MIP)-coated silica fibre. In this technique, a membrane molecular imprinted polymer coated silica microfiber was protected with toluene filled polypropylene hollow-fibre membrane. With this type of configuration the analytes were first extracted to the organic phase and then adsorbed on the MIP-coated silica microfiber. After the extraction the hollow membrane was removed and the analytes were desorbed from the microfiber by the usual procedure of SPME–HPLC commercial devices. This technique with HPLC–UV was applied to determine 6 triazines from sludge water and LODs were in the range of 0.006–0.020 $\mu g\,L^{-1}$ and RSD were 1.2–9.6%. The same research group developed special device to performance LLSME to overcome water-compatibility problem of the MIP-coated fibre, which integrated traditional LLE and SPME into one single operation [125]. This technique is a three-phase microextraction approach. It is fast, selective and sensitive pretreatment method for trace analysis of pesticides in complex aqueous samples.

Sanagi et al. [126] developed a novel microextraction technique, solid phase membrane tip extraction (SPMTE), involving the use of tiny cone-shaped membrane tip protected multi-walled carbon nanotubes (MWCNTs). This technique was evaluated for extraction of 4 triazines in river water samples prior to micro-LC–UV. The SPMTE device consisted of MWCNTs enclosed within a home-made cone-shaped polypropylene (PP) membrane attached to 1000 μL capacity pipette tip. The enriched analytes were desorbed by ultrasonication in 100 μL of acetonitrile. The LODs were in the range of 0.2–0.5 $\mu g\,L^{-1}$ and RSD were 5.7–8.5%. The SPMTE is advantageous in terms of short extraction time, low solvent usage, cost effective and easy to use. In the presence of the porous membrane as protection barrier, the technique could be used to extract analytes from complex matrices, such as wastewater and sludge samples.

3.9. Stir bar sorptive extraction (SBSE)

Another solvent-free technique is stir bar sorptive extraction (SBSE). Sorption usually takes place on a 1.5 cm long glass magnetic stirrer coated with a thick layer of polydimethylsiloxane (PDMS). Its sorption capacity is a hundred times greater in comparison with sorption capacity of SPME fibres. Because of the non-polar character of PDMS, the SBSE cannot be used to the extract strong polar compounds unless derivatization was utilized. In order to overcome this limitation, a new dual-phase stir bar was introduced by Bicchi et al. [127]. The new stir bar consisted of a short PDMS tube containing different carbon-based adsorbents. They showed enhanced extraction yield for polar compounds compared with those from conventional PDMS stir bar [128]. These new dual-phase twister was successfully applied to extraction of atrazine from spiked water sample [127].

Retained analytes are then desorbed thermally in a thermal desorption unit and transferred into GC injector, or desorbed with solvent extraction followed by using HPLC analysis. The parameters determining the efficacy of this kind of extraction include sample volume, extraction time and stirring speed [129]. Fig. 7 shows the stir bar sorption extraction setup.

Nakamura and Daishima [130] applied stir bar sorptive extraction (SBSE) thermal desorption (TD) coupled with GC–MS to determine 64 pesticides from various classes in river water samples. The LODs were in the range of 0.2–20 $ng\,L^{-1}$ and RSD were 1.4–20.2%. This technique has several advantages: a smaller sample size is required (about 10 mL), the sample preparation time is shorter, and eliminates use of solvent. Recently, to improve mass transfer of analytes, Richter et al. [131] proposed rotating disk sorptive extraction (RDSE) coupled with GC–MS to determine 3 OPP and 3 pyrethroids in river water samples. The extraction

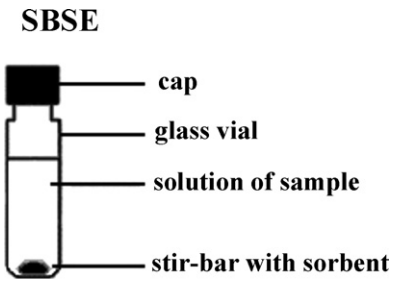

Fig. 7. The stir bar sorptive extraction setup.

device consisted of a Teflon disk (1.5 cm) containing 350 μL of immobilized PDMS phase on one of the surface of the disk. Under the optimized conditions, the LODs were in the range of 0.01–0.48 $\mu g\,L^{-1}$ and RSD were 10–20%. RDSE achieves a higher recoveries than SBSE, because of higher PDMS volume and higher surface area to volume ratio, which allows for improved mass transfer. The disadvantage of this technique requires long extraction time (up to 3 h), which largely depends on the polarity of the analytes. For the more apolar pesticides shorter extraction times are required.

The main objectives of sample preparation are the analyte preconcentration with simultaneous removal of potential interferents, if needed converting the analyte into a more suitable form for detection, and providing a robust and reproducible method independent of variations in the sample matrix. Recently, new objectives have been set such as using smaller sample sizes, minimize the amount of organic solvents, improvement of selectivity and facilitate to automation [132]. There are many widely used novel and improved techniques that require the use of minimal amounts of solvent, if any at all. But it is difficult to state definitively which of them is the most appropriate for extracting OPP + ONP from water samples, because each of them has specific advantages and disadvantages. Most of them ensure a high degree of preconcentration, so analytes present in trace amounts can be determined.

4. Final determination

The final stage of the analytical procedure is the identification of compounds and their quantitative determination using suitable instrumentation. Which technique should be used depends on the properties of the pesticides under scrutiny. One particular method of determination is usually applicable to pesticides with similar properties. In most cases chromatographic techniques are used in combination with suitable detectors, specific to a given group of compounds. The most frequently used are:

- capillary gas chromatography (GC), pesticides determined by GC should be volatile and thermally stable;
- high-performance liquid chromatography (HPLC), usually in reversed-phase mode, for pesticides that cannot be determined by GC, e.g. polar and thermally labile compounds, such as herbicides, carbamates and triazines, and other compounds that require derivatization [3].

The most commonly used technique is gas chromatography (GC) – equipped with a suitable detector sensitive to the determined analytes (e.g. MS, NPD, ECD, FPD, TSD). Another useful technique for the determination of OPP + ONP is a high performance liquid chromatography (HPLC) – equipped with usually UV and DAD detector.

The association of solventless and solvent-minimized sample preparation techniques to modern chromatographic methods,

Table 4
Methodologies for determining organophosphorus and nitrogen pesticides in different types of water samples.

Analytes	Matrix	Isolation and/or preconcentration technique	Final determination technique	Limits of detection	Recoveries	References
8 OPP	River water, pond water, tap water, well water	SPE	GC–NPD/FID	GC–NPD 50–130 ng L^{-1}; GC–FID 4.5–11.7 μg L^{-1}	93.8–104.5%	[28]
5 carbamates and 3 triazines	Drinking water, surface water	SPE	LC–ESI-MS	0.1–0.5 μg L^{-1}	65–97.8%	[31]
5 OPP	Drinking water	SPE	GC–MS	0.15–0.95 μg L^{-1}	–	[39]
82 pesticides from different classes, incl. ONP and OPP	Drinking water	MLLE	GC–ECD/NPD	<100 ng L^{-1}	>50%	[44]
8 ONP	River water	DLLME	GC–MS	0.021–0.12 μg L^{-1}	24.2–115.6%	[45]
3 ONP	Ground water	DLLME	GC–MS	0.003–0.04 μg L^{-1}	80.3–108.8%	[46]
13 OPP	Farmland runoff, well water, river water	DLLME	GC–FPD	3–20 ng L^{-1}	78.9–107%	[47]
3 ONP	Tap water and reservoir water	SPE–DLLME	GC–MS	0.002–0.006 μg L^{-1}	89–112%	[51]
4 OPP	Tap water, well water, rain and river water	IL-DLLME	HPLC–UV–VIS	0.1–5.0 μg L^{-1}	99.9–117.6%	[52]
8 phenylurea herbicides	River water	PDLLME	HPLC–UV	0.1–0.028 ng mL^{-1}	91.2–104.1%	[58]
1 OPP	Tap water, snow	VALLME	GC–μECD	3.2–10 ng L^{-1}	72.2–102.3%	[60]
7 OPP and 1 carbamate	Drinking water, river water	HF(2)ME	GC–FTD	0.001–0.072 μg L^{-1}	80–104%	[61]
4 OPP	Lake water	HF(2)ME	GC–MS	0.2–0.006 μg L^{-1}	83.1–107%	[62]
6 OPP	Wastewater	BN-HF(2)ME	GC–MS	0.3–11.4 ng L^{-1}	82–102%	[63]
7 triazines	River water	MASE	GC–MS	1–10 ng L^{-1}	60–90%	[65]
9 OPP and 7 triazines	Wastewater	MASE	GC–MS	2–10 ng L^{-1}	40–100%	[66]
1 OPP and 8 ONP	Lake water, river water and sea water	MMLLE	GC–MS	1.6–15 ng L^{-1}	–	[67]
5 sulfonylurea herbicides	Reservoir water, tap water and wastewater	MMLLE	CE	0.4 ng mL^{-1}	89–97%	[68]
9 OPP	Well water, sea water, tap water, farmland runoff, river water	LPME-SFO	GC–FPD	10–40 ng L^{-1}	96–104%	[69]
6 OPP	Lake water	SDME	GC–FPD	0.21–0.56 μg L^{-1}	77.7–113.6%	[71]
13 OPP	Well water, river water, farmland runoff	SDME	GC–FPD	1–5 ng L^{-1}	91–104%	[72]
10 OPP	Tap water, river water, lake water	SDME	GC–MS	0.01–0.073 μg L^{-1}	57–102%	[73]
7 triazines	River water	SDME	GC–MS	0.015–0.4 μg L^{-1}	80–90%	[74]
5 pesticides from different classes, incl. OPP and ONP	Reservoir water	CFME	HPLC–UV	0.6–4.0 ng mL^{-1}	77.2–106%	[76]
4 OPP and 4 triazines	Roof runoff, rain water, precipitation (rain, snow, hail)	SPE	GC–NPD	0.05 ng L^{-1}	–	[77–81]
28 pesticides from different classes, incl. ONP and OPP	Wastewater from olive washing	SPE	GC–TSD	1–3 ng L^{-1}	74–103%	[82]
4 OPP and 3 carbamates	Canal water, runoff	SPE	GC–MS	8.9–19.8 μg L^{-1}	–	[83]
2 OPP and 2 carbamates	Sewage water, ground water and surface water	SPE	LC–MS/MS	0.2–88.9 ng L^{-1}	50–115%	[84]
20 pesticides from different classes, incl. ONP and OPP	Pond water	SPE	GC–ECD/NPD	0.8–74.9 ng L^{-1}	60–120%	[85]
7 carbamates	Drinking water, surface water	SPME, SPE	GC–MS	SPME–GC/MS 0.6–19 μg L^{-1}; SPE–GC/MS 20–38 ng L^{-1}	–	[86]

Table 4 (*Continued*)

Analytes	Matrix	Isolation and/or preconcentration technique	Final determination technique	Limits of detection	Recoveries	References
12 pesticides from different classes, incl. ONP and OPP	Tap water	SPE	HPLC–UV	0.15–0.8 μg L^{-1}	85–107%	[87]
25 pesticides from different classes, incl. ONP and OPP	Drinking water	SPE	HPLC–APCI–MS	10–100 ng L^{-1}	63–110%	[88]
16 OPP	Ground water	MLLE, SPE	GC–FPD	MLLE–GC/FPD 5–100 ng L^{-1}; SPE–GC/FPD 1–6 ng L^{-1}	MLLE 15–117%; SPE 39–127%	[89]
31 pesticides from different classes, incl. 1 OPP and 5 carbamates	River water, treated water	SPE	LC–APCI–MS	10–250 μg L^{-1}	56.7–120%	[90]
1 OPP	Tap water	(MWCNTs) SPE	HPLC–UV	0.06 ng mL^{-1}	94.1–96.8%	[95]
1 OPP and 2 ONP	Tap water and reservoir water	(MWCNTs) SPE	Spectrophotometry (UV–VIS)	2–3 μg L^{-1}	84–104%	[96]
2 ONP	River water, reservoir water, tap water and wastewater	(MWCNTs) SPE	HPLC–DAD	9 and 33 ng L^{-1}	82.6–103.7%	[97]
3 ONP	Surface water and groundwater	(MWCNTs) SPE	GC–MS	0.02–0.05 μg L^{-1}	72.27–109.68%	[98]
1 OPP and 2 ONP	Tap water, reservoir water and stream water	(MWCNTs) SPE	HPLC–UV	37.5–220 ng L^{-1}	81–108%	[99]
2 ONP	Lake water, reservoir water and underground water	(MWCNTs) SPE	CE	0.36–0.4 μg L^{-1}	86–108%	[102]
6 OPP	Seawater and reservoir water	(OSWCNTs and OMWCNTs) SPE	GC–FPD	0.07–0.12 μg L^{-1}	79.1–101.9%	[103]
4 OPP	River water, tap water	MISPE	GC–NPD	10–32 ng L^{-1}	77.5–99.1%	[104]
OPP and 6 triazines	Ground water, drinking water	SPME	GC–TSD	OPP 1–30 ng L^{-1}; triazines 8–50 ng L^{-1}	77.4–131.7%	[105]
10 triazines	Surface water, ground water	SPME	GC–MS	2–17 ng L^{-1}	–	[106]
6 OPP	River water	SPME	GC–FPD	0.049–0.301 μg L^{-1}	75.3–102.6%	[107]
11 OPP	Surface water	SPME	GC–TSD	0.39–19.9 ng L^{-1}	–	[118]
6 triazines	Surface water	SPME	GC–MS	0.001–0.005 μg L^{-1}	93.2–106.2%	[119]
7 triazines	Tap water	MIP-SPME	GC–MS	14–95 ng mL^{-1}	93.6–99.8%	[122]
7 triazines	Tap water	MIP-SPME	GC–MS	20–90 ng mL^{-1}	96.3–99.6%	[123]
6 triazines	Sludge water	LLSME	HPLC–UV	0.006–0.020 μg L^{-1}	81.7–108.7%	[124]
4 triazines	River water	SPMTE	Micro-LC–UV	0.2–0.5 μg L^{-1}	95–101%	[126]
11 pesticides from different classes, incl. 1 OPP and 1 triazine	River water	SBSE	GC–MS	10–240 ng L^{-1}	42–96%	[129]
64 pesticides from different classes, incl. ONP and OPP	River water	SBSE	GC–MS	0.2–20 ng L^{-1}	58.5–132%	[130]
3 OPP and 3 pyrethroids	River water	RDSE	GC–MS	0.01–0.48 μg L^{-1}	76–101%	[131]
5 carbamates	Runoff from arable land, tap water	LPME	GC–MS	0.2–0.8 μg L^{-1}	83–127.9%	[133]
7 OPP	Subterranean water, sea water, river water, lake water	HS-SPME	GC–FTD/MS	10–40 ng L^{-1}	80–120%	[134]
1 OPP	Lake water, tap water	LPME	HPLC–DAD	10 μg L^{-1}	92.3–96.7%	[135]
6 carbamates	Preconcentrated sample of high-purity water	SPME	HPLC–UV	1–15 μg L^{-1}	97.3–100%	[136]
5 OPP	Sewage	Membrane extraction	GC–FID	0.26–2.37 μg L^{-1}	94–108%	[137]
8 OPP	Tap water, sea water, sewage	SPME	GC–NPD	6–136 ng L^{-1}	77–122%	[138]

such as gas chromatography high resolution mass spectrometry (GC–HRMS), fast GC, two-dimensional gas chromatography (GC×GC) and ultra high performance liquid chromatography (UHPLC), will be most likely a powerful option for the development of rapid and ultra-sensitive analytical methods. Table 4 lists some of the methodologies for determining OPP + ONP in different types of water samples.

Nowadays, the trend is to develop analytical methods enabling a broad spectrum of analytes to be determined in a single analytical run (MRM – multiresidue methods). But the problem here is that the compounds to be determined simultaneously, often present at low concentrations, have different physicochemical properties depending on their chemical structure. Such a methodology, apart from being able to determine a large number of compounds in one run, should:

- ensure maximum removal of interferents from extracts,
- give large recoveries of target compounds, high sensitivity and good precision,
- be environmentally friendly, i.e. require the smallest possible quantities of samples and chemical reagents, especially organic solvents,
- be cheap, quick and easy to carry out.

Research is continuing into the improvement of existing analytical methods and the development of new ones capable of supplying reliable results for a wide range of analytes.

5. Conclusions

The increasingly widespread application of pesticides means that ever larger amounts of them are entering the environment. Pesticides have various physical and chemical properties. As a result of various transformations in the environment, they may be converted into compounds of even greater toxicity. Nowadays they are regarded as some of the most hazardous pollutants of the environment because of their mobility and long-term action on living organisms. They are usually present in the environment in very low concentrations, in matrices of great complexity, which poses further problems in their analysis. The many laborious and time-consuming sample preparation steps that are required, themselves possible sources of additional contamination and error, prolong the time required for the determination of pesticides in the environment. That is why a special analytical procedure is required in this respect, one that enables a large number of compounds to be determined in a single analytical run. In many cases in the determination of pesticides, compounds have to be isolated from a complex matrix and then preconcentrated prior to the final determination. Analyses of this kind are recommended by the European Union. That is why studies are going on into the improvement of existing techniques and the development of new ones, which would enable pesticides from different chemical classes to be reliably and reproducibly determined at the same time in a quick, simple, cheap, effective and environmentally friendly manner. The improvements to existing techniques are aimed at their miniaturization and automation, and the use of solvent-free techniques at the sample preparation stage. The paper describes extraction techniques requiring the use of solvents – liquid–liquid extraction (LLE) and its modifications, membrane extraction techniques, hollow fibre-protected two-phase solvent microextraction, liquid phase microextraction based on the solidification of a floating organic drop (LPME-SFO), solid-phase extraction (SPE) and single-drop microextraction (SDME) – as well as solvent-free techniques – solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE).

6. Acronyms

Acronym	Full name
CFME	Continuous-flow microextraction
CNTs	Carbon nanotubes
CW	Carbowax
ECD	Electron capture detector
DAD	Diode array detector
DI	Direct immersion
DLLME	Dispersive liquid–liquid microextraction
DVB	Polydivinylbenzene
FPD	Flame photometric detector
FTD	Flame thermionic detector
GC	Gas chromatography
GC×GC	Two-dimensional gas chromatography
GC–HRMS	Gas chromatography–high resolution mass spectrometry
HF(2)ME	Hollow fibre-protected two-phase solvent microextraction
HPLC	High performance liquid chromatography
HS	Head space
IL	Ionic liquids
LLE	Liquid–liquid extraction
LLSME	Liquid–liquid–solid microextraction
LOD	Limit of detection
LPME	Liquid–phase microextraction
LPME-SFO	Liquid–phase microextraction based on the solidification of a floating organic drop
MASE	Membrane-assisted solvent extraction
MESCO	Membrane-enclosed sorptive coating
MIP	Molecularly imprinted polymer
MISPE	Molecularly imprinted solid-phase extraction
MLLE	Micro liquid–liquid extraction
MMLLE	Membrane micro liquid–liquid extraction
MRM	Multiresidue methods
MS	Mass spectrometry
MWCNTs	Multiwalled carbon nanotubes
NPD	Nitrogen-phosphorus detector
OCP	Organochlorine pesticides
OMWCNTs	Oxidized multiwalled carbon nanotubes
OPP + ONP	Organophosphorus and organonitrogen pesticides
OSWCNTs	Oxidized single-walled carbon nanotubes
PA	Polyacrylate
PDLLME	Partitioned dispersive liquid–liquid microextraction
PDMS	Polydimethylsiloxane
PEEK	Polyetheretherketone
PME	Polymer membrane extraction
POICS	Polar organic chemical integrative sampler
PP	Polypropylene
PS-DVB	Polystyrene-divinylbenzene
RDSE	Rotating disk sorptive extraction
RSD	Relative standard deviation
SBSE	Stir bar sorptive extraction
SDME	Single-drop microextraction
SPE	Solid-phase extraction
SPME	Solid phase microextraction
SPMTE	Solid phase membrane tip extraction
SWCNTs	Single-walled carbon nanotubes
TD	Thermal desorption
TRIMPS	Trimethylpentane-containing passive sampler
TSD	Thermionic specific detector
UHPLC	Ultra high performance liquid chromatography
UV	Ultra-violet
VALLME	Vortex-assisted liquid–liquid microextraction

References

[1] M. Biziuk, A. Przyjazny, J. Czerwiński, M. Wiergowski, J. Chromatogr. A 754 (1996) 103–123.
[2] A. Beyer, M. Biziuk, Ecol. Chem. Eng. 14 (2007) 35–58.
[3] M. Tankiewicz, J. Fenik, M. Biziuk, Trends Anal. Chem. 29 (2010) 1050–1063.
[4] M. Tankiewicz, M. Biziuk, Analityka 3 (2010) 46–50.
[5] Directive 2009/128/EC of the European Parliament and of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides, Off. J. Eur. Comm. L309 (2009).
[6] J. Namieśnik, Z. Jamrógiewicz, Fizykochemiczne metody kontroli zanieczyszczeń środowiska, WNT, Warszawa, 1998.
[7] M. Biziuk, Pestycydy, występowanie, oznaczanie i unieszkodliwianie, WNT, Warszawa, 2001.
[8] Regulation (European Commission) no. 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a Euro-

pean pollutant release and transfer register and amending Council Directives 91/689/EEC and 96/61/EC, Off. J. Eur. Comm. L33/1 (2006).
[9] 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. Comm. L327 (2000).
[10] Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration, Off. J. Eur. Comm. L372 (2006).
[11] WHO, Guidelines for drinking-water quality, third ed., World Health Organization, Geneva, 2008.
[12] C. Jorgensen, H.B. Boyd, J. Fawell, O. Hydes, Final Report on Establishment of a List of Chemical Parameters for the Revision of Drinking Water Directive, DHI, Denmark, 2008.
[13] Pesticide Action Network (PAN), www.panna.org (accessed 18.08.2011).
[14] Biuletyn Informacji Publicznej Ministerstwa Rolnictwa i Rozwoju Wsi, Tabela 1-Agregacja według rodzajów środków ochrony roślin, www.bip.minrol.gov.pl (accessed 18.08.2011).
[15] The Food and Environment Research Agency, Pesticide Statistic Usage, http://pusstats.csl.gov.uk/ (accessed 18.08.2011).
[16] G.W. Ware, D.M. Whitacre, The Pesticide Book, sixth ed., MeisterPro Information Resources, Willoughby, OH, 2004.
[17] U.S. Environmental Protection Agency (EPA), 2006–2007 Pesticide Market Estimates, http://www.epa.gov/opp00001/pestsales/07pestsales/table_of_contents2007.htm (accessed 18.08.2011).
[18] China Pesticide Suppliers Guide, http://focus.agropages.com/china/ (accessed 18.08.2011).
[19] Eurostat (European Commission), Statistic Database, Total Sales of Pesticides, http://epp.eurostat.ec.europa.eu/tgm/table.do;jsessionid=9ea7974b30db2e3cc7aa8fa349f58e8f9969e44dc10a.e34SbxiPb3uSb40Lb34LaxqRb3eRe0?tab=table&plugin=1&language=en&pcode=tag00084 (accessed 18.08.2011).
[20] M.L. Feo, E. Eljarrat, D. Barceló, Trends Anal. Chem. 29 (2010) 692–705.
[21] F. Ye, Z. Xie, X. Wu, X. Lin, Talanta 69 (2006) 97–102.
[22] United States Environmental Protection Agency, Registration Eligibility Decision for Permethrin, EPA 738-R-06-017, US EPA, Washington, 2006.
[23] Directive of the European Union 98/83/EC of 3.XII, 1998 R. on the Quality of Water Intended for Human Consumption, 1998, http://www.scribd.com/doc/8264629/Directive-9883EC-Drinking-water-standards (accessed 18.08.2011).
[24] S. Armenta, S. Garrigues, M. de la Guardia, Trends Anal. Chem. 27 (2008) 497–511.
[25] M. Tobiszewski, A. Mechlińska, B. Zygmunt, J. Namieśnik, Trends Anal. Chem. 28 (2009) 943–951.
[26] M. Farré, S. Pérez, C. Gonçalves, M.F. Alpendurada, D. Barceló, Trends Anal. Chem. 29 (2010) 1347–1362.
[27] F. Pena-Pereira, I. Lavilla, C. Bendicho, Trends Anal. Chem. 29 (2010) 617–628.
[28] E. Ballesteros, M.J. Parrado, J. Chromatogr. A 1029 (2004) 267–273.
[29] L. Alder, K. Greulich, G. Kempe, B. Vieth, Mass Spectrom. Rev. 25 (2006) 838–865.
[30] A. Lazartigues, C. Fratta, R. Bandot, L. Wiest, C. Feidt, M. Thomas, C. Cren-Olivé, Talanta 85 (2011) 1500–1507.
[31] J.M.F. Nogueira, T. Sandra, P. Sandra, Anal. Chim. Acta 505 (2004) 209–215.
[32] G. Gervais, S. Brosillon, A. Laplanche, C. Helen, J. Chromatogr. A 1202 (2008) 163–172.
[33] T. Hyötyläinen, J. Chromatogr. A 1153 (2007) 14–28.
[34] J. Namieśnik, Z. Jamrógiewicz, M. Pilarczyk, L. Torres (Eds.), Przygotowanie próbek środowiskowych do analizy, WNT, Warszawa, 2000.
[35] E. Łopuchin, J. Namieśnik Anal. 1 (2009) 29–36.
[36] A. Kot-Wasik, in: J. Namieśnik, W. Chrzanowski, P. Szpinek (Eds.), Nowe horyzonty i wyzwania w analityce i monitoringu środowiskowym, CEEAM, Gdańsk, 2003, pp. 563–570.
[37] A. Kot-Wasik, B. Zabiegała, M. Urbanowicz, E. Dominiak, A. Wasik, J. Namieśnik, Anal. Chim. Acta 602 (2007) 141–163.
[38] N. Sankararamakrishnan, A.K. Sharma, R. Sanghi, India Environ. Int. 31 (2005) 113–120.
[39] United States Environmental Protection Agency, Standardized Analytical Methods for Environmental Restoration Following Homeland Security Events – Revision 5.0, US EPA, Cincinnati, USA, 2009.
[40] H. Tse, M. Comba, M. Alaee, Chemosphere 54 (2004) 41–47.
[41] H. Sabik, R. Jeannot, J. Chromatogr. A 818 (1998) 197–207.
[42] Y.R. Tahboub, M.F. Zaater, Z.A. Al-Talla, J. Chromatogr. A 1098 (2005) 150–155.
[43] J.M. Kokosa, A. Przyjazny, M.A. Jeannot (Eds.), Solvent Microextraction, Theory and Practice, Wiley, New Jersey, 2009.
[44] A. Zapf, R. Heyer, H.J. Stan, J. Chromatogr. A 694 (1995) 453–461.
[45] D. Nagaraju, S.D. Huang, J. Chromatogr. A 1161 (2007) 89–97.
[46] R.S. Zhao, C.P. Diao, X. Wang, T. Jiang, J.P. Yuan, Anal. Bioanal. Chem. 391 (2008) 2915–2921.
[47] S. Berijani, Y. Assadi, M. Anbia, M.R. Milani Hosseini, E. Aghaee, J. Chromatogr. A 1123 (2006) 1–9.
[48] G. Wei, Y. Li, X. Wang, J. Sep. Sci. 30 (2007) 3262–3267.
[49] Q. Zhou, H. Bai, G. Xie, J. Xiao, J. Chromatogr. A 1188 (2008) 148–153.
[50] M. Rezaee, Y. Yamini, M. Faraji, J. Chromatogr. A 1217 (2010) 2342–2357.
[51] R.S. Zhao, Ch.P. Diao, Q.F. Chen, X. Wang, J. Sep. Sci. 32 (2009) 1069–1074.
[52] L. He, X. Luo, H. Xie, X.J. Ch. Wang, K. Lu, Anal. Chim. Acta 655 (2009) 52–59.
[53] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156–164.
[54] A.E. Visser, R.P. Swatloski, W.M. Reichert, S.T. Griffin, R.D. Rogers, Ind. Eng. Chem. Res. 39 (2000) 3596–3604.
[55] L.J. He, W.Z. Zhang, L. Zhao, X.S. Jiang, J. Chromatogr. A 1007 (2003) 39–45.
[56] X.H. Xiao, L. Zhao, X. Liu, S.X. Jiang, Anal. Chim. Acta 519 (2004) 207–211.
[57] M.I. Pinto, G. Sontag, R.J. Bernardino, J.P. Noronha, Microchem. J. 96 (2010) 225–237.
[58] T.Y. Chou, S.L. Lin, M.R. Fuh, Talanta 80 (2009) 493–498.
[59] E. Yiantzi, E. Psillakis, K. Tyrovola, N. Kalogerakis, Talanta 80 (2010) 2057–2062.
[60] Ch. Jia, X. Zhu, J. Wang, E. Zhao, M. He, L. Chen, P. Yu, J. Chromatogr. A 1217 (2010) 5868–5871.
[61] D.A. Lambropoulou, T.A. Albanis, J. Chromatogr. A 1072 (2005) 55–61.
[62] P.S. Chen, S.D. Huang, Talanta 69 (2006) 669–675.
[63] Ch. Basheer, A.A. Alnedhary, B.S.M. Rao, H.K. Lee, Anal. Chim. Acta 605 (2007) 147–152.
[64] J.Å. Jönsson, L. Mathiasson, Trends Anal. Chem. 18 (1999) 318–325.
[65] B. Hauser, P. Popp, E. Kleine-Benne, J. Chromatogr. A 963 (2002) 27–36.
[66] B. Hauser, M. Schellin, P. Popp, Anal. Chem. 76 (2004) 6029–6038.
[67] K. Lüthje, T. Hyötyläinen, M.L. Riekkola, Anal. Bioanal. Chem. 378 (2004) 1991–1998.
[68] Q. Zhou, J. Liu, Y. Cai, G. Liu, G. Jiang, Microchem. J. 74 (2003) 157–163.
[69] M.R. Khalili-Zanjani, Y. Yaminia, N. Yazdanfar, S. Shariati, Anal. Chim. Acta 606 (2008) 202–208.
[70] M.R. Khalili-Zanjani, Y. Yaminia, S. Shariati, J.Å. Jönsson, Anal. Chim. Acta 585 (2007) 286–293.
[71] Q. Xiao, B. Hu, Ch. Yu, L. Xia, Z. Jiang, Talanta 69 (2006) 848–855.
[72] F. Ahmadi, Y. Assadi, S.M.R. Milani Hosseini, M. Rezaee, J. Chromatogr. A 1101 (2006) 307–312.
[73] D.A. Lambropoulou, E. Psillakis, T.A. Albanis, N. Kalogerakis, Anal. Chim. Acta 516 (2004) 205–211.
[74] H. Bagheri, F. Khalilian, Anal. Chim. Acta 537 (2005) 81–87.
[75] D.A. Lambropoulou, T.A. Albanis, J. Biochem. Biophys. Methods 70 (2007) 195–228.
[76] Y. He, H.K. Lee, J. Chromatogr. A 1122 (2006) 7–12.
[77] Ż. Polkowska, M. Tobiszewski, T. Górecki, J. Namieśnik, Urban Water J. 6 (2009) 441–448.
[78] Ż. Polkowska, T. Górecki, J. Namieśnik, Chemosphere 49 (2002) 1275–1283.
[79] M. Grynkiewicz, Ż. Polkowska, T. Górecki, J. Namieśnik, Water Air Soil Pollut. 149 (2003) 3–16.
[80] Ż. Polkowska, A. Kot, M. Wiergowski, L. Wolska, K. Wołowska, J. Namieśnik, Atmos. Environ. 34 (2000) 1233–1245.
[81] M. Grynkiewicz, Ż. Polkowska, T. Górecki, J. Namieśnik, Chemosphere 43 (2001) 303–312.
[82] M.G. Rubio, A.R. Medina, M.I.P. Reguera, M.L. Fernández de Córdova, Microchem. J. 85 (2007) 257–264.
[83] S. El-Kabbany, M.M. Rashed, M.A. Zayed, J. Hazard. Mater. 72 (2000) 11–21.
[84] J.B. Baugros, B. Giroud, G. Dessalces, M.F. Grenier-Loustalot, C. Cren-Olivé, Anal. Chim. Acta 607 (2008) 191–203.
[85] M. Lyytikäinen, J.V.K. Kukkonen, M.J. Lydy, Arch. Environ. Contam. Toxicol. 44 (2003) 437–444.
[86] R.C. Martínez, C.G. Hermida, E.R. Gonzalo, L.R. Miguel, J. Sep. Sci. 28 (2005) 2130–2138.
[87] W. Liu, H.K. Lee, Talanta 45 (1998) 631–639.
[88] T.L. Potter, M.A. Mohamed, H. Ali, J. Agric. Food Chem. 55 (2007) 204–210.
[89] F.J. López, J. Beltran, M. Forcada, F. Hernández, J. Chromatogr. A 823 (1998) 25–33.
[90] J.Y. Hu, T. Aizawa, Y. Magara, Water Res. 33 (1999) 417–425.
[91] N. Fontanals, R.M. Marcé, F. Borrull, J. Chromatogr. A 1152 (2007) 14–31.
[92] N. Fontanals, R.M. Marcé, F. Borrull, Trends Anal. Chem. 24 (2005) 394–406.
[93] K.A. Wepasnick, B.A. Smith, J.L. Bitter, D.H. Fairbrother, Anal. Bioanal. Chem. 396 (2010) 1003–1014.
[94] K. Pyrzynska, Chemosphere 83 (2011) 1407–1413.
[95] H. Katsumata, T. Matsumoto, S. Kaneco, T. Suzuki, K. Ohta, Microchem. J. 88 (2008) 82–86.
[96] Y.D. Al-Degs, M.A. Al-Ghouti, A.H. El-Sheikh, J. Hazard. Mater. 169 (2009) 128–135.
[97] Q. Zhou, J. Xiao, W. Wang, G. Liu, Q. Shi, J. Wang, Talanta 68 (2006) 1309–1315.
[98] G. Min, S. Wang, H. Zhu, G. Fang, Y. Zhang, Sci. Total Environ. 396 (2008) 79–85.
[99] A.H. El-Sheikh, A.A. Insisi, J.A. Sweileh, J. Chromatogr. A 1164 (2007) 25–32.
[100] A.H. El-Sheikh, J.A. Sweileh, Y.S. Al-Degs, A.A. Insisi, N. Al-Rabady, Talanta 74 (2008) 1675–1680.
[101] M. Asensio-Ramos, J. Hernandez-Borges, L.M. Ravelo-Peréz, M.A. Rodriguez-Delgado, Electrophoresis 29 (2008) 4412–4421.
[102] V.H. Springer, A.G. Lista, Talanta 83 (2010) 126–129.
[103] Q. Li, X. Wang, D. Yuan, J. Environ. Monit. 11 (2009) 439–444.
[104] X. Zhu, J. Yang, Q. Su, J. Cai, Y. Gao, J. Chromatogr. A 1092 (2005) 161–169.
[105] C. Gonçalves, M.F. Alpendurada, J. Chromatogr. A 968 (2002) 177–190.
[106] Z. Yao, G. Jiang, J. Liu, W. Cheng, Talanta 55 (2001) 807–814.
[107] S. Frías, M.A. Rodríguez, J.E. Conde, J.P. Pérez-Trujillo, J. Chromatogr. A 1007 (2003) 127–135.
[108] P. Su, S.D. Huang, Talanta 49 (1999) 393–402.
[109] M. Natangelo, S. Tavazzi, R. Fanelli, E. Benfenati, J. Chromatogr. A 859 (1999) 193–201.
[110] C. Rocha, E.A. Pappas, Ch. Huang, Environ. Pollut. 152 (2008) 239–244.
[111] S. Magdic, A. Boyd-Boland, K. Jinno, J. Pawliszyn, J. Chromatogr. A 736 (1996) 219–228.

[112] D.A. Volmer, J.P.M. Hui, Arch. Environ. Contam. Toxicol. 35 (1998) 1–7.
[113] B.A. Tomkins, R.H. Ilgner, J. Chromatogr. A 972 (2002) 183–194.
[114] C. Gonçalves, M.F. Alpendurada, J. Chromatogr. A 1026 (2004) 239–250.
[115] C. Gonçalves, M.F. Alpendurada, J. Chromatogr. A 963 (2002) 19–26.
[116] M.T. Sng, F.K. Lee, H.Å. Lakso, J. Chromatogr. A 759 (1997) 225–230.
[117] C. Dietz, J. Sanz, C. Cámara, J. Chromatogr. A 1103 (2006) 183–192.
[118] W. Liu, Y. Hu, J. Zhao, Y. Xu, Y. Guan, J. Chromatogr. A 1102 (2006) 37–43.
[119] Ch. Basheer, S. Jegadesan, S. Valiyaveettil, H.K. Lee, J. Chromatogr. A 1087 (2005) 252–258.
[120] E. Turiel, A.M. Esteban, J. Sep. Sci. 32 (2009) 3278–3284.
[121] V. Pichon, F. Chapuis-Hugon, Anal. Chim. Acta 622 (2008) 48–61.
[122] D. Djozan, M. Mahkam, B. Ebrahimi, J. Chromatogr. A 1216 (2009) 2211–2219.
[123] D. Djozan, B. Ebrahimi, Anal. Chim. Acta 616 (2008) 152–159.
[124] Y. Hu, Y. Wang, Y. Hu, G. Li, J. Chromatogr. A 1216 (2009) 8304–8311.
[125] Y. Hu, T. Ye, Y. Yu, Y. Cao, Ch. Guo, J. Chromatogr. A 1218 (2011) 3935–3939.
[126] H.H. See, M.M. Sanagi, W.A.W. Ibrahim, A.A. Naim, J. Chromatogr. A 1217 (2010) 1767–1772.
[127] C. Bicchi, Ch. Cordero, E. Liberto, P. Rubiolo, B. Sgorbini, F. David, P. Sandra, J. Chromatogr. A 1094 (2005) 9–16.
[128] J. Chen, Ch. Duan, Y. Guan, J. Chromatogr. B 878 (2010) 1216–1225.
[129] A. Penálver, V. García, E. Pocurull, F. Borrull, R.M. Marcé, J. Chromatogr. A 1007 (2003) 1–9.
[130] S. Nakamura, S. Daishima, Anal. Bioanal. Chem. 382 (2005) 99–107.
[131] A. Giordano, P. Richter, I. Ahumada, Talanta (2010), doi:10.1016/j.talanta.2011.07.087.
[132] R.M. Smith, J. Chromatogr. A 1000 (2003) 3–27.
[133] J. Zhang, H.K. Lee, J. Chromatogr. A 1117 (2006) 31–37.
[134] D.A. Lambropoulou, T.A. Albanis, J. Chromatogr. A 922 (2001) 243–255.
[135] P. Liang, L. Guo, Y. Liu, S. Liu, T. Zhang, Microchem. J. 80 (2005) 19–23.
[136] Y. Gou, R. Eisert, J. Pawliszyn, J. Chromatogr. A 873 (2000) 137–147.
[137] Z. Sun, J.K. Hardy, Adv. Environ. Res. 4 (2000) 225–231.
[138] I. Valor, J.C. Moltó, D. Apraiz, G. Font, J. Chromatogr. A 767 (1997) 195–203.