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Solid-Phase Extraction for Enrichment and Separation of Herbicides

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1. Introduction

Herbicides are widely used for of broad-leaved weeds and other vegetation. They are relatively inexpensive and very potent even at low concentrations. The majority of herbicides are directly applied to soil or sprayed over crop fields and as consequence of large production and high stability, they are released directly into environment. For that, herbicides can enter as contaminants into streams, rivers or lakes directly from drainage of agricultural areas. The need for herbicide monitoring in natural water is essential for achieving good water quality objectives, because in most countries groundwater is the major source of drinking water. Moreover, the monitoring of herbicides in soil and crops is important in order to control their impact on the environment.

Recent studies have focused more on herbicide degradation/transformation products (from hydrolysis, oxidation, biodegradation or photolysis) because they can be present at greater levels in the environment than the parent herbicide and can sometimes be as toxic or even more toxic. New compounds have also come on the market (such as glyphosate, organophosphorus herbicides) and studies are being conducted to understand their fate and transport in the environment (Richardson, 2009).

Thus, it is important to develop a reliable and sensitive method for the simultaneous determination of such compounds in different kinds of samples. High-performance liquid chromatography with mass spectrometry or array diode detection are good options for herbicides monitoring (Cheng et al., 2010; Maloschik et al., 2010). Tandem mass spectrometry is usually used to confirm identification of selected herbicides. While LC-MS/MS methods are now predominantly used for pesticides and their degradation products, GC-MS methods are still occasionally used. For example, GC-MS was used by Hildebrandt et al. (2007) to measure 30 priority pesticides and their transformation products in agricultural soils and an underlying aquifer in the Ebro River Basin in Spain. The sensitivity of detection, however, is still not high enough in many cases for direct determination of herbicides at the level required by different regulations. Therefore, a preconcentration procedure for the analytes and clean-up steps must be applied for complex samples.

Solid-phase extraction (SPE) is the most popular sample preparation technique of environmental, food and biological samples and it already replaced the classic liquid-liquid extraction as the reduction or complete elimination of solvent consumption in analytical procedures, which is very important according to the rules of green chemistry (Camel, 2003;

Pyrzynska, 2003; Fontales et al., 2007). The main goal for application of SPE is to achieve isolation, preconcentration and clean-up of the sample in a single step. This can be achieved by an appropriate selection of the type of sorbent or their combination. For this reason the properties of the analytes, nature of matrix, the required trace-level concentration and the type of chromatography involved later in the separation step should be taken into consideration. The strategy of sample pretreatment in SPE-HPLC system is also guided by the method of final detection after chromatographic separation. Application of a simple detection mode, *e.g.* diode array UV, requires more selective isolation and enrichment. When the more specific quantification is used, such as fluorescence, mass spectrometry or electrochemical methods, application of SPE sample pretreatment can improve the limit of detection.

The extraction process depends on the type of sorbent used and retention is due to reversible hydrophobic, polar and ionic interactions between the analyte and the sorptive material. Sorption can be non-specific, in that case weak dispersive interactions such as van der Waals forces will dominate. However, sorbents utilizing specific interactions resulting from analyte polarity, ionic nature or the presence of specific functional groups are preferred. The classical sorbents in SPE are silica-based (Spivakov et al., 2006), carbonaceous materials (Kyriakopoulos & Doulia, 2006; Pyrzynska, 2008) or polymeric, primarily styrene-divinylbenzene copolymers (Fontanals et al., 2004; Kyriakopoulos & Doulia, 2006). The novel sorbents with improved selectivity towards the particular groups of compounds or even individual compounds includes immunosorbents (Haginaka, 2005) and molecularly imprinted polymers (MIP) (Dias et al., 2009; Lasáková & Jandera, 2009). Carbon nanotubes, a new form of carbon-based sorbents, are also promising materials in SPE of herbicides (Pyrzynska, 2008).

The objective of this chapter is to present the recent advances in the area of novel materials as solid phase extractors for herbicide analysis. The papers published over the last five years are discussed in more detail. The emphasis is also given to the application of several SPE systems for automated preparation of environmental, food and biological samples.

2. Classic sorbents

Silica chemically bonded with various groups has been the most common material for SPE. This sorbent can be classified as reversed-phase sorbent with octadecyl (C₁₈), octadecyl (C₈), ethyl (C₂) and phenyl or as normal-phase sorbent with cyanopropyl, aminopropyl and diol functional groups. Their interaction mechanisms are mainly based on hydrophobic interaction (van der Waals forces), thus these SPE packing provide high recoveries for nonpolar analytes. Nevertheless, silica-based sorbents are unstable at extremes pH (2 > pH > 8), and they have relatively low capacity and low recovery for basic analytes. Several types of modifications were used to immobilize different compounds on the surface of classical silica-based sorbents to increase their selectivity (Parida et al., 2006; Kailasam et al., 2009). New materials based on poly(methyltetradecylsiloxane) and poly(methyloctylsiloxane) thermally immobilized onto the silica support have been tested for extraction of some herbicides (Vigna et al., 2006; Faria et al., 2007). Liu (2008) had used silica gel coated with gold nanoparticles self-assembled with alkanethiols for the extraction of steroidal compounds.

The bonded-silica sorbent may be packed in different formats: filled microcolumns, cartridges or discs. A variety of bonded-silica phases are commercially available in the

cartridge format. Extraction could be also performed with membrane disks containing C₁₈-bonded silica (8 µm particles) on polytetrafluoroethylene or glass fiber supports (Spivakov et al., 2006; Li et al., 2006). Disc provides shorter sample processing time on account of their larger cross-sectional area and decreased pressure drop, allowing higher sample flow rates. This is important for environmental samples, where larger sample volumes are usually employed to achieve adequate detection limits.

The polymeric sorbents based on styrene-divinylbenzene exhibit higher capacity and better chemical stability over the whole pH range in comparison with bonded silica. Due to the specific π - π interactions they are relatively selective for analytes with aromatic rings. The use of highly crosslinked polymeric sorbents with their specific surface up to 800 m²/g or hypercrosslinked polymeric sorbents (over 1000 m²/g) could improve the analytes retention as more π - π sites in the aromatic rings will then be accessible to interact with the analytes (Ahn et al., 2006).

3. Hydrophilic and mixed-mode polymeric sorbents

The hydrophobic nature of classical sorbents leads to poor retention of polar compounds. To overcome these problems, the research in new SPE materials has been recently focused on the development of hydrophilic and mixed-mode polymeric materials. Such sorbents combine high specific surface area and polar interaction between sorbent and analyte due to introduction of the polar moiety to the polymer structure.

3.1 Hydrophilic polymeric sorbents

The hydrophilic polymeric sorbents are obtained by chemical modification of the existing hydrophobic materials or by copolymerisation of monomers that contain suitable functional groups. The polar substituents reduce the interfacial tension between the polymer surface and aqueous sample improving the wetting characteristics and increase contact between the analyte and polymeric sorbent. Strata-X (styrene skeleton modified with a pyrrolidone group) and Oasis HLB (macroporous poly(*N*-vinylpyrrolidone-divinylbenzene) copolymer) are the most common hydrophilic sorbent used in the herbicides extraction (Stoob et al., 2005; D'Archivio et al., 2007, Polati et al., 2006; Mazzella et al., 2008; Yu et al., 2009). Most of the studies investigate the performance of Oasis HLB in off-line SPE using different cartridge size available (from 30 to 500 mg). Other studies employ the direct coupling of on-line SPE to HPLC with column switching technique (Xu et al., 2007) or 96-well plate (Morihiya et al., 2008) to obtain high sample throughput. Absolut Nexus, the methacrylate and divinylbenzene copolymer has been recently applied in clean-up of complex samples, such as biological matrices with the subsequent extraction of analytes (Rodriguez-Gonzalo et al., 2009).

Biesaga et al. (2005) compared the recoveries of chlorophenoxy acidic herbicides using various SPE cartridges (C₁₈, Strata-X, Oasis HLB, SAX and phenyl-silica). The better performance of Strata-X, Oasis and phenyl-silica sorbents in comparison with silica gel C₁₈ can be attributed to their aromatic structure, which can interact with aromatic analytes *via* π - π interactions (Fig. 1). Additionally, Oasis HLB cartridges are water-wettable, and thus there is no need to ensure that it remains wet before loading the aqueous sample. The recovery of dicamba, the least hydrophobic compound evaluated, was much lower; only its sorption on Strata-X reached 74%.

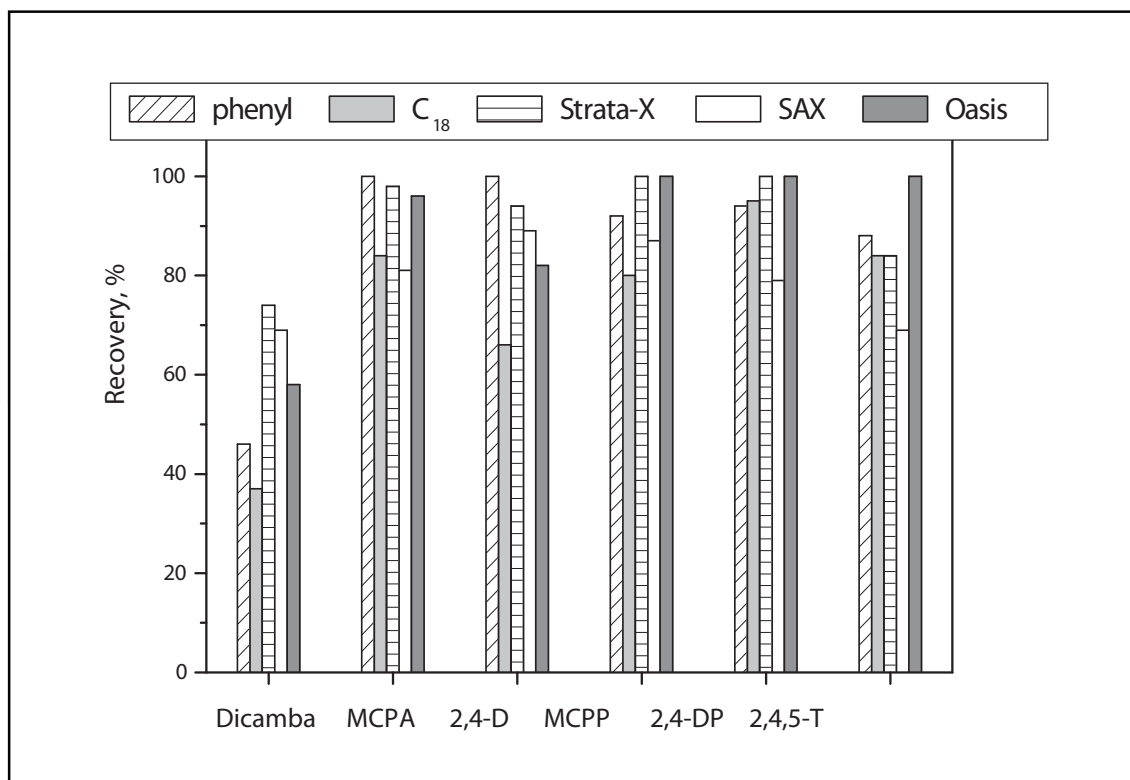


Fig. 1. Recoveries of chlorophenoxy acids extracted from 10 mL of deionized water spiked at the 5 µg/L level using various SPE cartridges. (Adopted from Biesaga et al., 2005).

3.2 Mixed-mode polymeric sorbents

Mixed-mode polymeric sorbents combine the polymeric skeleton with ion-exchange groups, thus these hybrid materials rely upon two types of interactions mechanism for their performance: reversed-phase and ion-exchange (Fontanals et al., 2010). Careful selection of the polymeric skeleton (which enhances the reversed-phase interactions) and the ionic groups (which tune the ion-exchange interactions) could give the combination of two highly desirable properties in solid phase extraction (i.e. retentivity and selectivity) in one single material. The benefit of the ion-exchange capacity is that either analytes, the matrix components or even the ionization state of the sorbent (in the case of weak-exchange resins) can be switched during the different steps in SPE procedure. It allows the interference elimination in the washing step and eluting the analytes more selectively, just by suitable pH combination in each step.

Mixed-mode sorbents are classified as cationic or anionic, and as strong or weak ion exchange, depending on the ionic group attached to the resin. Each of these groups is designed to extract selectively analytes with certain chemical properties (i.e. strong/weak acidic or basic). However, the selectivity of the extraction process depends on choosing not only a suitable sorbent but also a suitable SPE protocol (Fontanals et al., 2010).

Oasis MCX and Oasis MAX have the same as Oasis HLB skeleton (polyvinyl pyrrolidone-divinylbenzene) modified chemically with sulfonic acid and quaternary amine groups, respectively. These mixed-mode sorbents are mainly applied for extraction of analytes (charged or not) from complex biological and environmental matrices (Rosales-Conrado et al., 2005; Sorensen et al., 2008; Rodriguez-Gonzalo et al., 2009).

Lavén et al. (2009) proposed a novel solid phase extraction method whereby 15 basic, neutral and acidic compounds from wastewater were simultaneously extracted and subsequently separated into different fractions. This was achieved using mixed-mode cation- and anion-exchange SPE (Oasis MCX and Oasis MAX) in series. For less complex samples, e.g. the active-sludge-treatment effluent water, Oasis MCX used alone may be an alternative method. Although sewage treatment plant influent waters containing high loads of organic compounds, the clean-up step using only Oasis MCX was insufficient, leading to unreliable quantitation. Utilising the ability to separate compounds by mixed-mode SPE according to basic and acidic functionalities should be also very useful in the characterisation of unknown water contaminants.

4. Molecularly imprinted polymers

Molecularly imprinted polymers (MIPs) are highly crosslinked polymers with specific binding sites for a particular analyte. The print molecule – called the template – is chemically coupled with one or several functional monomers and then spatially fixed in a solid polymer by the polymerisation reaction. After template removal by extraction, polymers with imprints, which are complementary to the template in terms of size, shape and functionality are obtained. These polymers are able to rebind selectively the template molecule or its structural analogues. The right selection of functional monomers is important in molecular imprinting because the interactions with functional groups affect the affinity of MIPs (Lasáková & Jandera, 2009). Molecular modelling can be used to predict which functional monomers are capable to form effective polymers as some monomers have a natural affinity to some herbicides (Breton et al., 2007).

Two principally different approaches to molecular imprinting may be distinguished. In non-covalent (or self-assembly) approach the imprint molecule complexes the monomers by non-covalent or metal ion coordination interactions. The covalent imprinting employs reversible covalent bonds and usually involves a prior chemical synthesis step to link the monomers to the template. The first approach is more flexible in the range of templates that can be used but covalent imprinting yields better defined and more homogeneous binding sites. Moreover, the former is practically much easier, since complex formation occurs between template and monomers in a solution. Figure 2 shows this entire process schematically and more details on the preparation of imprints can be found elsewhere (Diaz-Garcia & Lamo, 2005; Qiao et al., 2006; Dias et al., 2009). It should be stressed that some monomers have natural affinity to some herbicides (Breton et al., 2007). The retention on blanks seems to be a good reflection of the relative affinity of monomers to the herbicides, and this interaction must be naturally strong enough to allow the binding enhancement by a MIP. Proper selection of reagents, reaction medium and conditions should take into consideration the complexity of selective sites formation in the polymer structure to obtain a material capable of not only highly selective recognition of target analytes but also having good kinetic parameters (Kloskowski et al., 2009). Kopohpaei et al. (2008) proposed a chemometric approach for the optimization of the main factors affecting the material structure and the molecular recognition properties of the MIPs.

Tamayo et al. (2005) found that the use of 2-(trifluoromethyl) acrylic acid as functional monomer leads to the synthesis of polymers with higher capacities and affinity constants for phenylurea herbicides in comparison with metacrylic acid when isoproturon was used as template. Thus, the simultaneous extraction of several herbicides was possible since each

compound was able to interact with specific binding sites in the presence of related compounds. However, both linuron and metabromuron were clearly displaced by the other analytes in the competition experiments and were able to interact only with a very small number of binding sites.

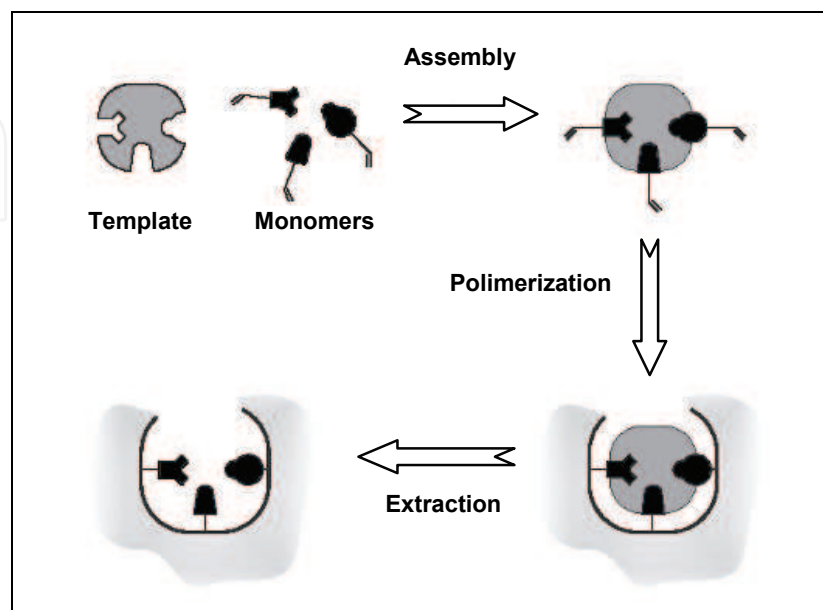


Fig. 2. Schematic representation of molecular imprinting principle.

Most of the reported studies concern the development of MIPs for one target analyte only, but basically similar compounds that are present in samples, can also be recognized and extracted (Chapuis et al., 2003). Herrero-Hernandez et al. (2007) demonstrated the applicability of an imprinted polymer obtained using bisphenol-A as template for the determination of several xenobiotic compounds in honey samples. It was found that MIP was able to extract selectively phenols and several phenoxyacids, while no-specific recognition of other compounds such as atrazine, chlortoluron, carbaryl and diuron herbicides was also observed.

MIPs can be obtained in the format of particles, coatings, monolayers of selective compounds bound to the surface of support, monolithic packings or fibers (Oxelbark et al. 2007). A fast and straightforward method for preparation and binding study of solid phase microextraction (SPME) fiber on the basis of atrazine- and ametryn-imprinted polymers has been proposed (Djozan & Ebrahimi, 2008; Djozan et al., 2009). The fabricated fibers were thermally and chemically stable and flexible enough to be placed in home-made SPME syringe and to be inserted directly into GC injection port.

Porous self-supported MIP membranes with developed inner surface have been proposed for atrazine enrichment (Sergeyeva et al.; 2007). It was shown that the MIP particles demonstrated significantly less pronounced imprinting effect and lower adsorption capabilities as compared to the MIP membranes of the same composition. MIPs could be also incorporated into the acceptor phase of a microporous membrane liquid-liquid extraction system for preconcentration and clean-ups step before chromatographic analysis (Mhaka et al., 2009; Hu et al., 2009).

Recent applications of MIP-SPE technique for herbicide analysis are presented in Table 1.

Template	Monomer/ cross linker/ solvent	Analytes	Sample	References
2,4,5-trichloro phenoxyacetic acid	4-vinyl pyridine/ EGDMA/ methanol -water (3+1, v/v)	Chlorinated phenoxyacids	River water	Baggiani et al., 2004
Metsulfuron methyl	4- or 2-vinyl pyridine/EGDMA/ acetonitrile	Sufonylurea herbicides	Tap water	Bastide et al., 2005
Linuron or isoproturon	MAA or TFMAA/ EDMA/ toluene	Phenylurea herbicides	Corn sample extracts	Tamayo et al., 2005
Propazine	MAA/EGDMA/ CH ₂ Cl ₂	Triazines	Soil, vegetable extracts	Cacho et al., 2006
Cyanazine	MAA/EGDMA/ toluene	Cyanazine, atrazine	Waters	Breton et al., 2006
Atrazine or ametryn	MAA or TFMAA or 4-vinyl pyridine /EGDMA/toluene	Chlorotriazine and methyl thiotriazine herbicides	River water	Sambe et al., 2007
Atrazine	MAA/EGDMA/ toluene	Atrazine	Ground waters	Prasad et al., 2007
Phenoxyacetic acid	4-vinyl pyridine /methanol+water (1+1, v/v)	Phenoxyacetic herbicides	Waters	Zhang et al., 2007
Atrazine	MAA/ TEDMA/ DMF	Triazine herbicides	Waters	Sergeyeva et al., 2007
Ametryn	MAA/EGDMA/ acetonitrile	Ametryn	Standards	Koohpaei et al., 2008
Atrazine	MAA/ EGDMA/ acetonitrile	Triazine herbicides	Waters, rice, onion	Djozan et al., 2008
Bisphenol-A	4-vinyl pyridine /EGDMA/toluene	Phenoxyacetic herbicides	Honey	Herrero-Hernández et al., 2009
Ametryn	MAA/ EGDMA/ acetonitrile	Triazine herbicides	Drinking waters	Koohpaei et al., 2009
Atrazine	MAA/ EGDMA/ acetonitrile	Triazine herbicides	Food samples	Mhaka et al., 2009

MAA - methacrylic acid; EGDMA - ethylene glycol dimethacrylate; TFMAA - 2-(trifluoromethyl) acrylic acid; DVB - divinylbenzene; CH₂Cl₂ - dichloromethane; TEDMA - tri(ethylene glycol) dimethacrylate; DMF - dimethylformamide

Table 1. Recent applications of MIP-SPE technique for herbicide analysis

The analytical procedure based on molecularly imprinted SPE was developed for the determination of several triazine herbicides in soil and vegetable samples (Cacho et al., 2006). These samples has proven to be difficult to clean with a non-covalent imprinted polymer, making necessary the inclusion of an additional clean-up step to remove polar matrix components that prevented the final accurate quantification of target analytes. Figure 3 shows the chromatograms obtained with and without SPE procedure of soil (Fig.

3A) and potato (Fig. 3B) sample extracts spiked with 50 ng/g and 20 ng/g of triazine herbicides, respectively. As can be observed, the direct determination of triazines without clean-up was not possible due to interferences appearing in the chromatograms whereas it could be easily determined after cleaning sample extract using MIPs. The detection limits for the analysis ranged from 0.4 to 2.4 ng/g depending upon the herbicide, low enough to allow the environmental monitoring of triazines at concentration level below the established maximum residue limits by current legislation.

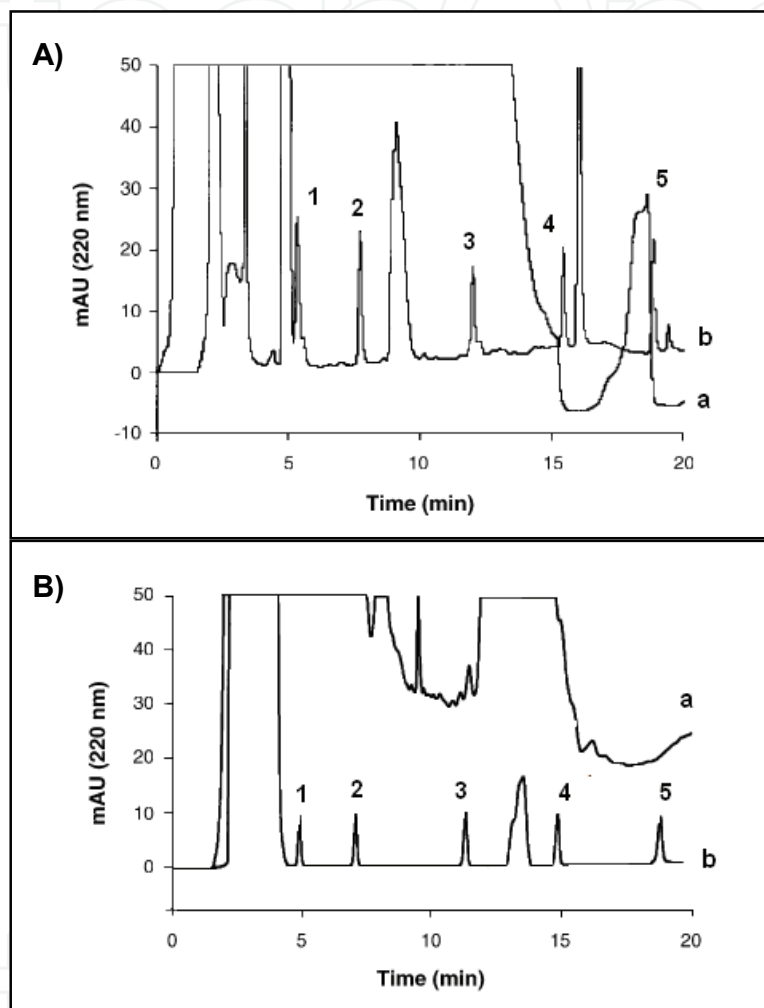


Fig. 3. Chromatograms obtained without (a) and with (b) SPE-MIP of soil (A) and potato (B) samples extracts spiked with triazine herbicides (50 and 20 ng/g, respectively). Peaks: 1-desisopropylatrazine; 2-desethylatrazine; 3-simazine; 4-atrazine; 5-propazine. Adopted from Cacho et al. (2006).

5. Carbon nanotubes

Carbon nanotubes (CNTs) represent the novel carbon-based nanomaterials with unique properties such as high surface areas, large aspect ratios, remarkably high mechanical strength as well as electrical and thermal conductivities. They can be described as a graphite sheet rolled up into a nanoscale-tube. Two structural forms of CNTs exist: single-walled (SWCNTs) and multi-walled (MWCNTs) nanotubes. CNT lengths can be as short as a few

hundred nanometers or as long as several microns. SWCNT have diameters between 1 and 10 nm and are normally capped at the ends. In contrast, MWCNT diameters are much larger (ranging from 5 nm to a few hundred nanometers) because their structure consists of many concentric cylinders held together by van der Waals forces (Wepasnik et al., 2010).

The characteristic structures and electronic properties of carbon nanotubes allow them to interact strongly with organic molecules, *via* non-covalent forces, such as hydrogen bonding, π - π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions. These interactions as well as hollow and layered nanosized structures make them a good candidate for application as a sorbent. The surface, made up of carbon atoms hexagonal arrays in graphene sheets, interacts particularly strongly with the benzene rings of aromatic compounds.

Oxidation of CNTs with nitric acid is an effective method to remove the amorphous carbon, carbon black and carbon particles introduced by their preparation process (Yang et al., 2006). It is known that oxidation of carbon surface can offer not only more hydrophilic surface structure, but also a larger number of oxygen-containing functional groups, which increase the ion-exchange capability of carbon material. Gas phase oxidation of activated carbon increases mainly the concentration of hydroxyl and carbonyl surface groups, while oxidation in the liquid phase increases particularly the content of carboxylic acids (Dastgheib & Rockstraw, 2002). The amount of carboxyl and lactone groups on the CNTs treated with nitric acid was higher in comparison to the process conducted using H_2O_2 and $KMnO_4$ (An & Zeng, 2003). Datsyuk et al. (2008) found that the nitric acid (65%) treated carbon nanotubes under reflux conditions for 48h suffered very high degree of degradation such as nanotube shortening and additional defect generation in the graphitic network. Functional groups can change the wettability of CNTs surfaces and consequently make them more hydrophilic and suitable for sorption of relatively low molecular weight and polar compounds. On the other hand, functional groups may increase diffusional resistance and reduce the accessibility and affinity of CNTs surfaces for organic compounds (Cho et al., 2008).

Recent applications of carbon nanotubes for removal and enrichment of herbicides in different types of samples are presented in Table 2. Earlier reports were discussed in the review papers (Pang & Xing, 2008; Pyrzyńska, 2008).

The comparison of carbon nanotubes, activated carbon and C_{18} silica in terms of analytical performance, application to environmental water, cartridge re-use, adsorption capacity and cost of adsorbent has been made for propoxur, atrazine and methidathion herbicides (El-Skeikh et al., 2008). The adsorption capacity of CNTs was almost three times higher than that of activated carbon and C_{18} , while activated carbon was superior over the other sorbents due to its low cost.

A comparative study suggested that carbon nanotubes had a higher extraction efficiency than Oasis HLB for the extraction of methamidophos and acephate, particularly for seawater samples (Li et al., 2009). Figure 4 presents the chromatograms of six organophosphorus pesticides in the spiked seawater sample extracted using CNTs and Oasis HLB sorbent. For other tested polar organophosphorus pesticides (dichlorvos, omethoate, monocrotophos and dimethoate) improvement was not significant, thus CNTs could supplement Oasis HLB for these compounds extraction.

Zhou et al. (2007) compared the trapping efficiency of CNTs and C_{18} packed cartridge using sulfonyleurea herbicides as the model compounds. When the matrices of the samples were very simple, such as tap water and reservoir water, the enrichment performance between

Analytes	Sample	Eluent	Recovery %	Reference
Sulfonylurea herbicides	Waters	Acetonitrile	80 - 105	Zhou et al., 2007
Atrazine and its metabolites	Water, soil	Ethyl acetate	72-109	Min et al., 2008
Organophosphorous herbicides	Fruit juices	Dichloromethane	73 -103	Ravelo-Perez et al., 2008
Various herbicides	Natural waters	Acetonitrile	81 - 108	El-Sheikh et al., 2008
Pirimicarb, pyrifenoxy, penconazol, cyprodynil, carbendazim,	Mineral water	Dichloromethane with formic acid (5% v/v)	53 - 94	Awensio-Ramos et al., 2008
Chloroacetanilide herbicides	Tap, river water	Ethyl acetate	77 -104	Dong et al., 2009
Triazine herbicides	Water	Acetonitrile/methanol (50%, v/v)	84-104	Al-Degs et al., 2009
Sulfonylurea herbicides	Environmental waters	Acetonitrile + 1% acetic acid	79 - 102	Niu et al., 2009
Organophosphorus herbicides	Seawater	Acetone or methanol	79 - 102	Li et al., 2009

Table 2. Recent applications of carbon nanotubes for removal and enrichment of herbicides

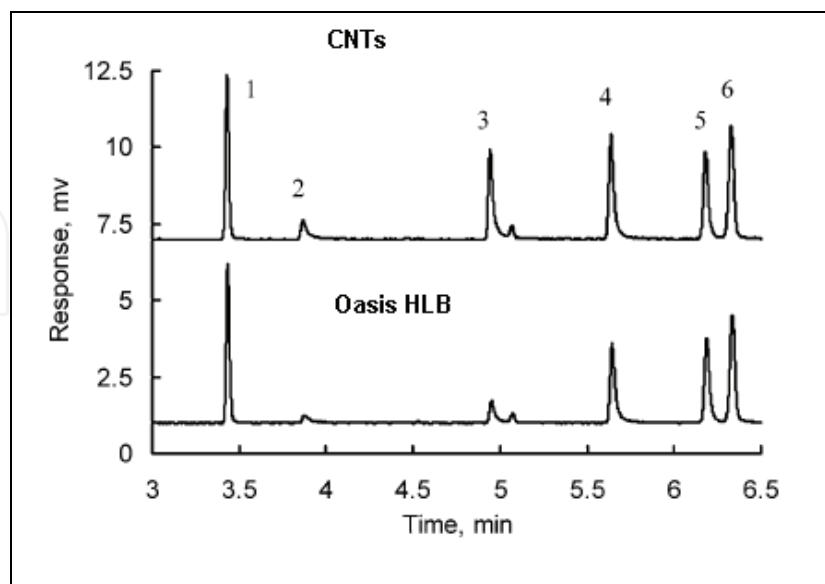


Fig. 2. Chromatograms of organophosphorus pesticides (1.0 $\mu\text{g/L}$) in the spiked seawater extracted with CNTs and Oasis HLB. Peaks identification: 1-dichlorvos, 2-methamidophos, 3-acephate, 4-omethoate, 5-monocrotophos, 6-dimethoate. Adapted from Li et al. (2009).

these two adsorbents had no significant difference. However, carbon nanotubes become much more suitable to extract herbicides from complex matrices (seawater and well-water). Carbon nanotubes could be also used in a format of disc. Incorporating sorbents of small particle size, the disc format possesses a larger surface area than the cartridge, resulting in good mass transfer and fast flow rates (Niu et al., 2009). To enhance the sorption capacity of the disks, double or even triple disks were used together. A comparison study showed that the double-disk system (comprising two stacked disks with 60 mg of CNTs) exhibited extraction capabilities that were comparable to those of a commercial C₁₈ disk with 500 mg sorbent for nonpolar or moderately polar compounds. The triple layered CNTs disk system showed good extraction efficiency when the sample volume was up to 3 000 mL (Niu et al., 2008).

Carbon nanotubes with high porosity and large adsorption area seems to be a good candidate for solid phase microextraction coating. Rastkari et al. (2009) proposed a novel coating by attaching CNTs onto a stainless steel wire through organic binder. The results showed that the CNTs fiber exhibited higher sensitivity and longer life span (over 150 times) than the commercial carboxen/polydimethylsiloxane coating.

6. On-line preconcentration

Solid phase extraction could be performed on-line by direct connection to the chromatographic system, therefore fully automated technique could be utilised. Hyphenated on-line SPE-HPLC systems are designed to improve not only sensitivity and selectivity of determination but also reduced sample manipulation and time, better intra- and inter-day reproducibility, higher sample throughputs as well better precision due to lower human participation, but typically requires the use of program controlled switch valves and column reconfiguration (Segura et al., 2007; Viglino et al., 2008). The extraction sorbents include mainly disposable cartridges, restricted access media, large-size particle and monolithic materials (Xu et al., 2007).

The valve setup for on-line SPE is presented in Fig. 3. The column-switching valve is used to direct the flow from the extraction column either to waste or to the HPLC analytical column. At the beginning of each run, the SPE column is conditioned. In the load position, sample is directly loaded in the loop and then preconcentrated, while matrix components are removed during the washing step. The valve is then switched, so that appropriate solution can elute the analytes from the extraction column onto the analytical column, when they are separated prior detection. After elution, the valve is switched back to its original position to wash and re-equilibrate the extraction column.

To improve the detection limit of column-switching system, the analytes should be preconcentrated from larger sample volume. Nevertheless, this would only be achieved if the analytes do not break through the SPE column. Garcia-Ac et al. (2009) estimated the breakthrough volumes of three herbicides (atrazine, cyanazine, simazine) and two of their transformation products (deethylatrazine and deisopropylatrazine) for several on-line SPE columns made of different sorbent materials. It was found that Strata-X was the best candidate for the preconcentration of large volume samples and all studied polymeric phases showed higher breakthrough volume than silica-based phases. The preconcentration of 10 mL sample lowered the limit of detection by a factor of 5 for atrazine, deethylatrazine and simazine, while for deisopropylatrazine the improvement factor was > 10.

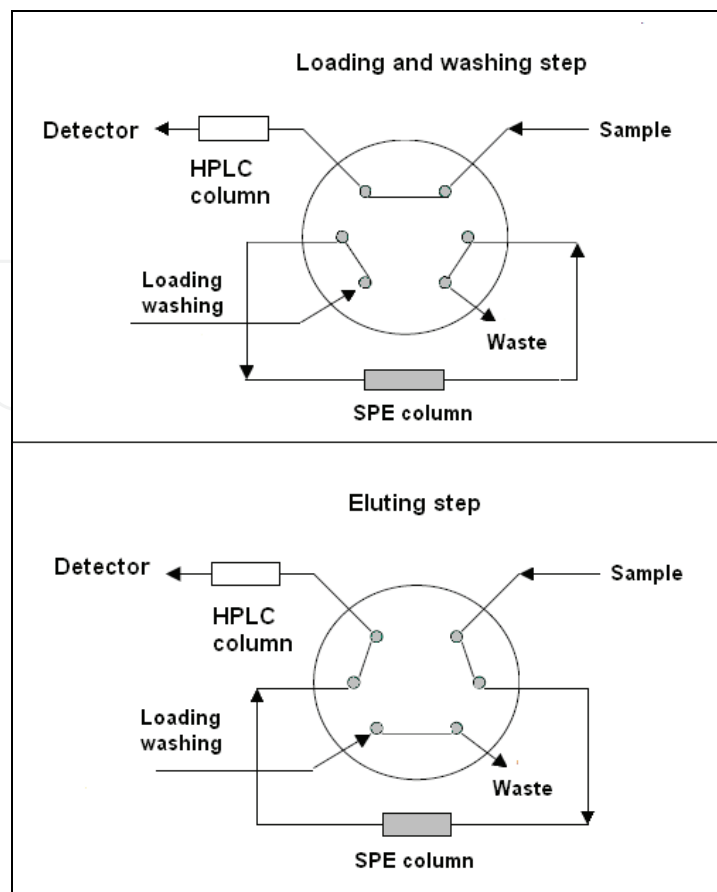


Fig. 3. Schematic diagram of valves configuration for on-line SPE-HPLC system.

The extraction column is treated as a permanent component of the flow network, being used repeatedly for the sample-loading and elution sequences, and being replaced or repacked only after long-term operation. The repeated use of sorbents may progressively affect their retention capabilities due to contamination or deactivation. Also, if the retained species are not totally eluted from the sorbent medium, this leads to carry-over effects between consecutive runs. An alternative to overcome these drawbacks relies on a surface-renewal scheme, the so-called SI-bead injection, where the contents of the SPE column are withdrawn on-line and replaced for each analytical run (Miró & Hansen, 2006). This approach was used for determination of chlorotriazine herbicides and primary monodealkylated metabolites in untreated complex environmental samples (e.g, ground waters from domestic rural wells and soil extracts). An automatic tandem-column multimodal-bead injection approach combining two types of sorbent beads (water-compatible MIP and reversed-phase mixed-mode Oasis HLB) was developed prior to on-line LC separation (Boonjob et al., 2010). The limit of detection for analysis of spiked water at the 0.5 $\mu\text{g}/\text{L}$ level was in the range of 0.02 - 0.04 $\mu\text{g}/\text{L}$ and overall procedure reproducibility within 1.4 - 5.5% RSD.

7. Quality control

Together with the fast development of analytical methodologies, the great importance is now attached to the quality of the measurement data. Many important decisions are based on measurements, thus good-quality analytical results are essential. The key property of

reliable results is their metrological traceability to stated references with a well established evaluation of the measurement uncertainty (Quevauville, 2004). In practice, method validation is done by evaluating series of method-performance characteristics, such as linearity, operating range, recovery, limit of detection and quantification, precision, selectivity and calibration. The relevant information in the fields of analytical method validation and quality assurances have been published (Taverniers et al., 2004; Gonzalez et al., 2004).

Matrix Reference Materials (MRM) are essential tools for the analytical protocols validation. The feasibility study of a MRM for the analysis of triazines and phenylurea herbicides in water was carried out (Deplagne et al., 2006). Different types of candidates MRM were prepared: solutions of pesticides diluted in acetonitrile and stored in sealed vials or stored at the dry state after the solvent evaporation to dryness, pesticides stored on two different types of polymeric sorbents (Oasis HLB and ENVI-Chrom P) after the percolation of drinking or river water spiked with herbicides. The stability of compounds stored at various temperatures was studied over a period of approximately one year. During the storage, some samples of each different MRM candidate were monthly analyzed by HPLC. Regarding the choice of materials for storage, it was found that a careful control of the temperature of evaporation to dryness is not necessary and similar results were obtained for recovery of herbicides for both used sorbents. All herbicides, except simazine, stored as a dry residue at room temperature exhibited a decrease in concentration of more than 20%. The stability seemed to be better when vials were stored at 0.5 °C and at -18 °C neither degradation nor loss of herbicides was observed. This study showed satisfactory long term stability (more than one year) at low temperature for herbicides stored in acetonitrile in vials and for herbicides concentrated on SPE cartridge obtained after passing through a water sample containing these analytes.

To evaluate behavior of these materials containing herbicides, a collaborative study including 15 laboratories has been organized (Mrabet et al., 2006). Observed reproducibility on candidate materials (after the removal of extreme results) was 16.1% for the vials with pesticides in acetonitrile (at around 0.125 mg/L) directly analyzed, 29.2% for a water sample spiked with the pesticides (at around 0.5 µg/L) analyzed after preconcentration on the cartridge and 26.7% for the cartridges previously percolated with the water containing the pesticides (250 mL at around 0.5 µg/L for each pesticide) analyzed after elution.

8. Conclusion

Several hundred herbicides of different chemical structure are used world-wide in agriculture. Due to their persistence, polar nature and water solubility, they are dispersed in the environment and their residues and transformation products are present in several environmental matrices. With increasing public concerns for agrochemicals and their potential movement in the ecosystem, many countries have severely restricted the maximum acceptable concentration of herbicides in drinking water and in vegetable foods. Therefore, the availability of sensitive, selective, precise and rapid analysis methods is essential. Herbicide residue analysis generally requires several steps such as extraction from the sample of interest, removal of interfering co-extractives, analytes enrichment and quantification of their content.

Solid-phase extraction is the top sample-extraction technique for liquid samples, since it can efficiently extract different types of analytes from their matrices and enrich them. Among

other advantages, SPE is versatile because a variety of sorbents is available, and the extraction can be tuned depending on how these sorbents interact with the analytes. In recent years, research into new kind of sorbents has focused on improving their capacity and selectivity. Mixed-mode polymeric sorbents, molecularly imprinted polymers and carbon nanotubes are among the new kind of sorbents, which could be useful in enrichment and clean-up purposes in herbicide analysis. MIPs are more selective than mixed-mode sorbents; however, mixed-mode sorbents have greater capacity than MIPs. Carbon nanotubes have a strong adsorption affinity for a wide variety of organic compounds, including pesticides, and are also characterized by their high sorption surface. The use of carbon-encapsulated magnetic nanoparticles avoids the time-consuming column passing and filtration operation and shows great analytical potential in preconcentration of large volumes of real water samples (Zhao et al., 2008). Application of carbon nanostructures have been facilitated by the improvement in their production as the cost has been a main factor in limiting commercialization. However, it is widely believed that if production volumes increase, cost would decrease markedly, thereby significantly increasing the utilization of the excellent properties of nanostructured carbon. Recently, new solvent-free process for producing CNTs from used polymers *via* thermal dissociation in the closed reactor under the inert or air atmosphere has been proposed (Pol & Thiyagarajan, 2010).

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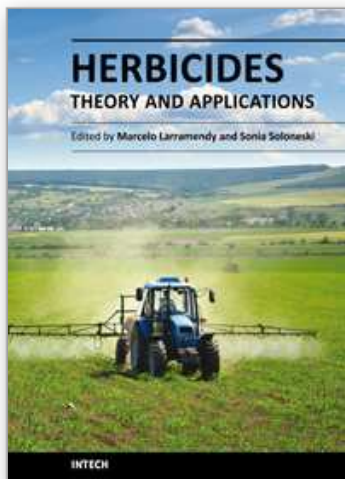
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The content selected in Herbicides, Theory and Applications is intended to provide researchers, producers and consumers of herbicides an overview of the latest scientific achievements. Although we are dealing with many diverse and different topics, we have tried to compile this "raw material" into three major sections in search of clarity and order - Weed Control and Crop Management, Analytical Techniques of Herbicide Detection and Herbicide Toxicity and Further Applications. The editors hope that this book will continue to meet the expectations and needs of all interested in the methodology of use of herbicides, weed control as well as problems related to its use, abuse and misuse.

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