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Molecularly imprinted polymers for the determination of organophosphorus pesticides in complex samples

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Abstract

Organophosphorus compounds constitute an important class of pesticides whose the toxicity of which arises from the inhibition of the acetylcholinesterase enzyme. They exhibit a wide range of physico-chemical properties, thus rendering their determination in complex oil samples particularly difficult. To facilitate their analysis at the trace level in various samples (environmental waters, soils, vegetables...), molecularly imprinted polymers (MIPs) that are synthetic polymers possessing specific cavities designed for a target molecule have been prepared. Often called synthetic antibodies, MIPs can replace antibodies in different application fields. Indeed, as immunosorbents, MIPs can be used as selective sorbents for the solid phase extraction of target analytes from complex matrices or as recognition elements in sensors. Their synthesis, characterization and use as selective sorbent for the selective recognition of organophosphorus pesticides have been already largely described and are summarized in this review.

Key words: organophosphorus pesticides; molecularly imprinted polymer; solid-phase extraction; sensors; trace analysis.

1. Introduction

The increasing use of pesticides for agricultural purposes cause serious risks to the human and animal health. Organophosphorus pesticides (OPPs) are among the most used pesticides. As mentioned in a recent review related to their analysis in fruit and vegetables, they are found mutagenic, carcinogenic, cytotoxic, genotoxic, teratogenic and immunotoxic [1]. Their determination, at very low concentration levels in environmental samples and foodstuff, constitutes a real analytical challenge. Indeed, OPPs exhibit a wide range of physico-chemical

properties thus explaining the possibility to analyze some of them either by gas chromatography (GC) for the most volatile compounds or by liquid chromatography (LC) for the most polar ones. For their analysis through GC, different types of detectors have been used including some specific detectors such as flame photometric detector (GC-FPD) or nitrogen phosphorus detector (NPD) and mass spectrometers for their identification capabilities [1,2]. These recent years, OPPs analysis through LC have been carried out in association with mass spectrometry (LC-MS) with regard to its higher sensitivity and identification capabilities, as compared to UV detection [1–3]. However, despite the advances in the development of such highly sensitive analytical instruments including high resolution mass spectrometry that can be associated with different ionization sources, a pre-treatment is usually necessary in order to extract and isolate the analytes of interest from complex samples before their determination [2].

The analysis of pesticide residues, including OPPs in environmental samples (waters, soils, sediments...), foodstuffs and biological fluids has been often reviewed, showing that numerous extraction methods have been developed for the treatment of solid and liquid samples those last ten years. Some of these reviews have focused on the development of various methods for the treatment of a given type of samples such as water samples [4], foodstuffs [5,6], such as fruits and vegetables [7], fatty vegetable matrices [8], foods of animal origin [9], olive and olive oil [10], baby-food [11] and honey using various techniques [12]. Others have reported the potential of a method or a group of close methods for the treatment of various types of samples such as solid-phase based extraction method for food and environmental samples [13], stir bar sorptive extraction (SBSE) for fruits and vegetables [14], single drop liquid extraction (SDLE) for waters and fruit juices [15] or liquid-phase micro-extraction for water samples including SDLE and dispersive liquid-liquid extraction [16], matrix solid phase dispersion (MSPD) for foodstuffs such as vegetables [17] or food from animal origin [17,18].

Despite the use of these efficient extraction and clean-up methods, matrix components are unavoidably present in final extracts thus causing a risk of matrix effect during GC or LC determination [19,20]. The effects caused by these matrix components can be reduced by improving the chromatographic resolution as can be achieved using multidimensional chromatography or by improving the selectivity during the sample treatment.

Selectivity, during sample pretreatment, can be obtained by using sorbent able to retain compounds by a molecular recognition mechanism. For this, it comes therefore possible to use immunoaffinity supports (i.e. immunosorbents, ISs) based on the use of specific antibodies that target a molecule of interest. The high selectivity and affinity of the antigen-antibody interactions allows a selective clean-up to being reached with high enrichment factors as already demonstrated for numerous pesticides in complex samples [21] including OPPs from water samples [22]. Other selective supports, called oligo-sorbents, have been recently proposed using aptamers immobilized onto a solid support. Aptamers are oligonucleotides with a specific sequence able to bind a given molecule with the same affinity as antibodies. Aptamers were recently successfully applied to the selective extraction of different target analytes from biological fluids and food samples [23,24]. A DNA sequence was previously described for the recognition of OPPs but not applied yet to their extraction from real samples [25]. Once the sequence is available, developing an oligosorbent is less expensive than an IS. However, despite their high potential, a limited number of sequences is, to date, available. This molecular recognition mechanism can also be exploited using molecularly imprinted polymers (MIPs)

that are synthetic polymeric materials possessing specific cavities designed for a template molecule. MIPs are often called synthetic antibodies in comparison with IS. They offer some advantages including easy, cheap and rapid preparation and high thermal and chemical stability [26]. The use of MIPs as selective sorbents for solid-phase extraction (SPE) is recent. It was initially proposed by Sellergren *et al.* in 1994 for extracting pentamidine present at low concentration in urine [27]. Since this first application, numerous MIPs were developed for the selective extraction of target analytes from complex samples [28–31]. Because of their high selectivity, they have been also already successfully used in several other fields such as sensors [32–34], bioassays [35,36] and enantiomeric separation [37].

Their synthesis, characterization and use as selective sorbent for the selective recognition of OPPs have been already largely described and mainly developed to be integrated in sensors or used in solid phase extraction. **Fig. 1a** gives an idea of illustrates the proportions of the application of MIPs for the determination of OPPs in these different fields. As shown by **Fig. 1b**, this field of research is very active since more than 70% of the papers have been published those last five years.

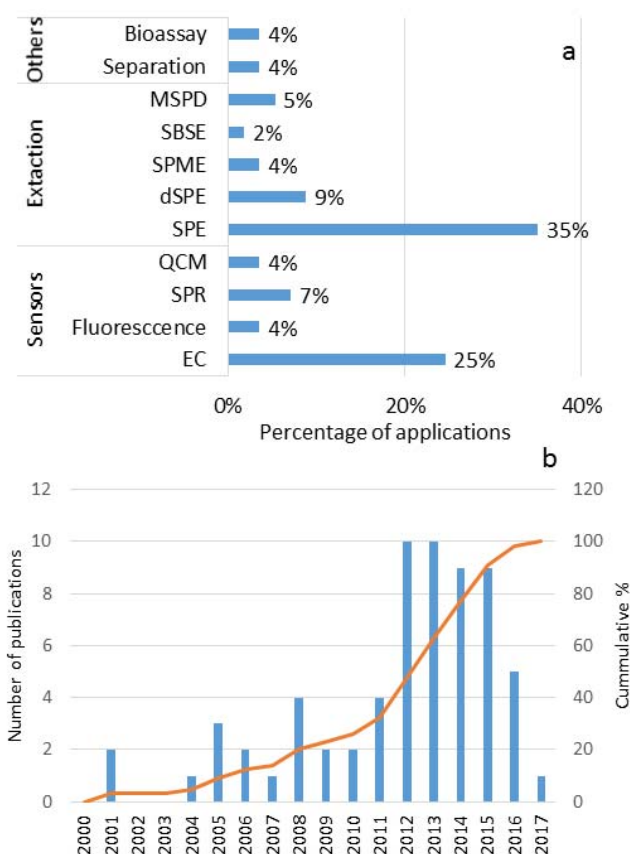


Fig. 1: Percentages of use of MIPs in the different fields such as sensors of different types e.g. piezoelectric (using using quartz cristal microbalance (QCM) or surface plasmon resonance (SPR)), optical (i.e. fluorescence) or electrochemical (EC)), as extraction sorbent in conventional SPE, in dispersive mode applied to liquid samples (dSPE) or solid samples (matrix solid-phase dispersion, MSPD), in micro-solid-phase extraction (SPME), in stir-bar solid-phase extraction (SBSE) or as stationary phase for separation purposes or in bioassays (a) and

cumulative percentages (red curve) of publications related to the development of MIPs for dedicated to OPPs (b).

Therefore, this review focuses on the presentation of polymerization methods used to produce MIPs for OPPs, their characterization in pure media and their performance as SPE sorbents or as selective tools of sensors for the determination of OPPs in real samples.

2. Synthesis of MIPs.

In the common approach, the synthesis of molecularly imprinted polymers (MIPs) involves first the solution complexation of a template molecule with functional monomers, through non-covalent bonds, followed by polymerization of these monomers around the template with the help of a cross-linker in the presence of an initiator. The choice of the chemical reagents making the MIP must be judicious in order to really create specific cavities designed for the template molecule. For these reasons, a monomer is chosen to develop strong interactions with the target analyte, i.e. an OPP or a structural analog acting as the template, in a porogen solvent. By the presence of a cross-linker, the polymerization takes place around the template. The template molecule is then removed, producing a polymer with binding sites complementary to the template in size, shape and position of the functional group. The conditions of synthesis of MIPs for OPPs (polymerization mode, reagents used), as reported in the literature, are summarized in **Table 1**.

As shown in this table, MIPs were prepared by radical polymerization of organic acrylate of acrylic based monomers. In most of the cases, a conventional bulk polymerization is achieved and gives rise to a monolith that has to be ground and sieved to obtain particles that present an heterogeneous size distribution. This procedure is easy to achieve but it is time-consuming and its yields are less than < 50%, mainly explained by the loss of MIP, as fine particles removed during a sedimentation step. In order to obtain more regular and homogeneous beads or microspheres, MIPs can also be prepared by precipitation polymerization that results from an increased amount of porogen or by more sophisticated methods such as suspension polymerization or multi-step swelling or surface-grafting. It was also proposed to develop MIPs by the hydrolysis and the condensation of organo-silanes around the template, thereby thus giving rise to a hybrid sol-gel material. This synthesis achieved in aqueous media presents the advantages to facilitate the dissolution of polar templates.

As shown by data reported in Table 1, more than 20 different OPPs were used as template molecule, the most frequently reported OPP templates being chlorpyrifos, parathion, parathion methyl, dimethoate and monocrotophos. The structure of the main studied OPPs and their log P values are reported in supplementary material (S1).

The use of a structural analog has been proposed to prepare MIPs for other chemicals to decrease the cost of the material when the target molecule is expensive and/or toxic as it can be the case for some toxins. It is also a way to circumvent the risk of residual template leaking from the polymer that may cause erroneous results when applying the MIP to trace analysis. Indeed, the complete removal of the template from the MIP after its synthesis can be difficult to achieve and necessitates extensive washing steps. The use of this molecule, named “dummy molecule”, that can be distinguished from the target analysis during its determination in real

samples, particularly by chromatographic methods when the MIP is used as extraction sorbent, constitutes an easy way to limit the risk caused by this leaking. The dummy molecule must resemble the target analyte in terms of shape, size and functionalities to obtain cavities that are able to bind the target analyte. This dummy approach was reported by different groups to produce OPP MIPs [48,49,60,63,80], including the use of a metabolite of OPPs, *i.e.* DETP [50].

As for other molecules, the most common approach used for the development of OPP MIPs for extraction purposes, consists of a non-covalent imprinting. To exploit the polar functions of the OPPs during the polymerization reaction, polar organic monomers such as MAA, AAM, 4-VP and IA were selected. For the same reasons, the solvent of polymerization was a weakly polar and aprotic solvent such as dichloromethane, chloroform and acetonitrile.

As mentioned by some authors, the selection of the monomer(s) and the template/monomer(s) ratio can be carried out by studying the changes in UV spectra of the template when adding increasing concentration of the monomer in the solvent selected for the synthesis [67,69,77]. Other spectroscopic methods were used such as NMR to highlight the presence of hydrogen bonds between the template and MAA [39,67,69,72,73] and FT-IR to highlight the interactions between OPP and OH-group of MAA [39,46,55,61,70,76,80,91,97,98,102]. This method was also used to control the template removal by comparing MIP spectrum before and after its washing [64,93,99], this control being most of the time ensured by analyzing the template amount in the washing solution by UV detection or by chromatographic analysis.

Computational design was also proposed to simulate monomer-template interactions and then to select the best monomer, *i.e.* the monomer that gives the highest interaction energy with the template [39,56,65,67] or to elucidate the best template/monomer ratio [79]. It was reported that results obtained using this approach, despite its high potential, must be confirmed by retention measurements (HPLC, SPE profiles) [56,81] or binding experiments [71] thus implying the synthesis of several MIPs with a selection of templates and/or monomers selected by the simulation.

3. MIP characterization

The potential of a MIP is related to the occurrence of selective cavities that promote a high interaction with the target OPP. In most of the works, a non-imprinted polymer (NIP) is synthesized in the same conditions as the MIP but without in the absence of the template. This control polymer, that does not possess any cavities, is studied in parallel during the MIP characterization. Because of the use of the same monomers, *porogen*...the nature of the interactions developed between a MIP and a template is the same as between the NIP and the template. The difference between the two sorbents is the strength of these interactions. If well-defined cavities were created during the polymerization step, the strength of the interactions is higher on the MIP than on the NIP because the template can be retained by different points (sum of the interactions) due to the spatial complementarities between the template and the cavities.

The first evaluation of the synthesized MIPs may consist in characterizing by SEM the surface of MIP/NIP [39,54,77,78,97,102], the shape and size of particles [50,58,59,79,98]. BET adsorption method can also be used to measure and compare the porosity of MIP/NIP [64].

Binding tests that consist in introducing a given amount of MIP/NIP in the presence of a known amount of an OPP and then measuring, after a fixed time, the amount retained by the MIP and the NIP was used to select the best monomer [49,59,82], the template/monomer ratio [49,51,59]. In these cases, the solvent used is very close or similar to the solvent used for the synthesis of the polymers to favor the same interactions as those developed during the polymerization step to create the cavities. The adsorption isotherm resulting from these binding experiments also allows, by using different models (Langmuir, Freundlich, Langmuir-Freundlich), the number of binding sites and their affinity towards the template molecules [80,93] and, in some cases, towards structural analogs to being defined [55,60,64,69,70,76,79,82,86,90,99].

Binding experiments were also carried out in a pure solvent, very similar to the nature of the sample matrix, such as aqueous buffer or pure water or acetonitrile for the further analysis of OPPs in aqueous or acetonitrile vegetable extracts, respectively [50,51,76,80,93,99]. These binding experiments were also carried out in heptane, the chosen solvent to dilute oil samples [58]. This approach allows a better evaluation of the retention potential and of the selectivity that can be expected in real samples to being better assessed. In the same way, by testing different solvents by binding experiments, the solvent that favors the highest selectivity can then be used to dilute the sample or sample extracts [65,78]. On the opposite, the solvent that gives the lowest affinity can be chosen as eluting medium in SPE procedure [78].

The effect of the nature of solvents on the retention properties was also studied by HPLC measurements. Indeed, this method was used to evaluate the solvent that favors the retention [56,72] and to evaluate the selectivity towards different analogs [56].

4. MIP for selective extraction

As already demonstrated by numerous reviews related to the development of MIPs for the selective extraction of compounds [28,103–106], this field of application is very active and represents more than half of the developments of MIPs for OPPs as shown by Fig. 1. Since the pioneer work of Sellergren in 1994 [27] who developed and used a MIP as SPE sorbent for the selective extraction of pentamidine from urine, different extraction devices are now envisaged. Indeed, despite the large use of MIP as solid-phase extraction sorbent (MIP-SPE), after its packing into disposable cartridges to carry out exhaustive extraction, beads of MIP were dispersed in liquid samples and solid sample to develop selective dispersive SPE (dSPE) or selective matrix solid-phase extraction (MSPD) methods, respectively. Other non-exhaustive extraction methods such as solid-phase micro-extraction (SPME) or stir-bar sorptive extraction (SBSE) have been developed for the selective trapping of OPPs from various types of samples [31,103,104]. These different developments are summarized in **Table 2**.

4-1- MIP-SPE of OPPs

As shown by the conditions of synthesis reported in **Table 2**, MIPs for SPE were mainly prepared by bulk polymerization. The resulting monolith was ground to obtain 25-50 μm

particles that were packed between two frits in disposable cartridges and applied as conventional SPE sorbent (C18 silica, polymers...) to the extraction of OPPs from real samples. Except in one case for which three OPPs were studied as template before eventually choosing omethoate as template [81], the reported works described the use of a unique OPP to prepare a MIP for this molecule and then for its selective extraction from real samples.

In more than 75% of the reported studies, MAA was used as monomer without any preliminary studies related to the selection of this monomer. The computational screening of monomers was only reported by Bakas *et al.* [65,71,81] that allows them to select a unique monomer that presents the highest interaction energy with the template. In one of these studies, several MIPs were synthesized using the several selected monomers (IA, MAA, TFMAA) and SPE was carried out to definitively select IA, since leading to a MIP that provides the highest retention and the best selectivity for omethoate [81].

In most of the cases, the presence of specific cavities was proven by binding experiments in a pure solvent spiked with increasing amounts of the target molecule. These experiments allow the affinity of the binding sites of the MIP to being compared with those of the NIP and then to evaluate the presence of specific cavities in the MIP. This approach was also used by Zhu *et al.* to evaluate the best monomer and solvent among three to produce cavities of high affinity for monocrotophos [77].

If binding experiments can also be used to determine the affinity of the MIP towards other OPPs [67,77], the ability of a MIP to trap several OPPs has been mainly done by measuring extraction recoveries on MIP and on NIP after the application of a SPE procedure previously optimized by studying the target compound alone. In a SPE procedure, different parameters can be studied such as (i) the nature of the percolated solution that must favor the retention, (ii) the composition of the washing solution that constitutes a key parameter for differentiating to differentiate the MIP from and the NIP and (iii) the nature and the volume of the elution solution to recover the target analyte. This is particularly well illustrated with the results reported by Bakas *et al.* [65] and related to the selective extraction of fenthion and four other OPPs from olive oil using a MIP produced with fenthion as template and AAM as monomer in dimethylformamide. After studying the retention of fenthion on MIP/NIP in different solvents, heptane was selected for its ability to favor the retention of this compound on MIP and different solvents were further tested as washing solvent to select the one that allows the retentions of between MIP and NIP to being differentiated. As shown by results reported in Fig. 2, the use of dichloromethane allows fenthion to being partially removed from the NIP (40%) during the washing step (**Fig. 2A**) while maintaining the retention on the MIP (**Fig. 2B**). To improve the selectivity of the procedure, an increasing amount of acetonitrile was added in dichloromethane. This study showed that the use of 5% acetonitrile in dichloromethane (v/v) allows 98% fenthion to being removed from the NIP (**Fig. 2C**) while maintaining its retention on the MIP (**Fig. 2D**).

This procedure optimized with fenthion was applied to four other OPPs and results, reported in **Table 3**, showed that it was possible to extract both fenthion and fenthion sulfoxide with recovery rates above higher than 93% and with a high selectivity, these compounds being not retained on the NIP. In return, the three other OPPs were not retained by the MIP.

This low ability of the MIPs to recognize a large number of OPPs was reported by numerous groups after this optimization with the MIP and the NIP in pure media [58,65,70,73,81]. This can be explained by the fact that the phosphate group of OPPs is substituted by very different

chemical groups as shown by the structure reported in Supplementary material (S1). In this case, the recognition of fenthion sulfoxide was certainly favored by the fact that it comprises, as fenthion, an aromatic group unlike the three other studied compounds. The effect of the structural similarity on the ability of a MIP to recognize selectively three OPPs was demonstrated by Sanagi *et al.* who developed a MIP using quinalfos as template. This MIP was able to selectively extract quinalfos but also diazinon and chlorpyrifos, *i.e.* three molecules that comprise an aromatic ring with one or two linked nitrogen atoms [97].

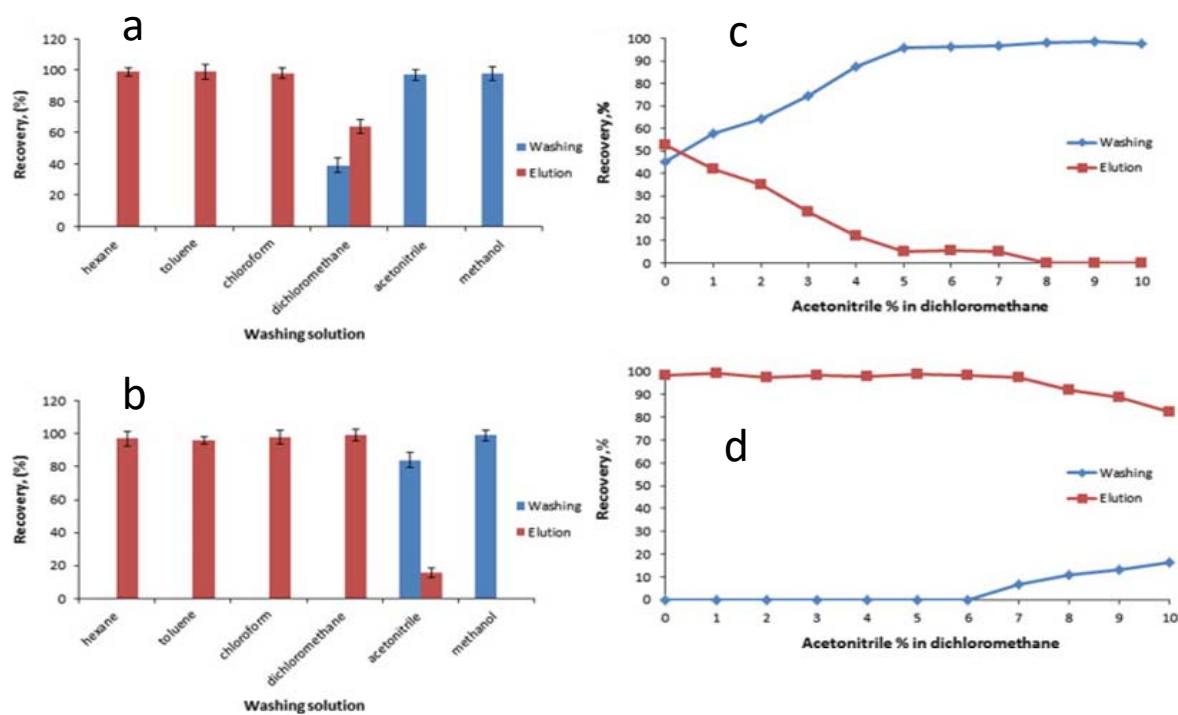


Fig. 2 : Recovery of fenthion in the washing (blue) and elution (red) fractions after loading 1 mL of 1 mg L⁻¹ pesticide on NIP (a,c) and MIP cartridges (b,d). Washing step: 2 mL of the solvents (a,b) or with different % of acetonitrile in dichloromethane (c,d); elution step: 1 mL of methanol/2% TFA [65].

Some authors reported the ability of the MIP to extract up to six OPPs with high recovery rates but the NIP was not used in parallel to the MIP when optimizing the SPE procedure [42,50,61,68,76,80]. In these conditions, the retention was certainly favored by the solvent selected as percolating medium but the real selectivity, believed to be brought by the cavities of the MIP, was not really proven.

To ensure the simultaneous trapping of two OPPs, *i.e.* monocrotophos and trichlorfon, from vegetable extracts with a high efficiency, two tailor-made MIPs were prepared using each target as template [76]. These MIPs were prepared by applying very similar conditions of synthesis to ensure the possibility to develop a unique extraction procedure based on the same chemical interactions. The authors just adapted the amount of each MIP to be introduced in the cartridge to ensure a high recovery of extraction for both molecules. To reach the same objective, a MIP

was prepared using both molecules, monocrotophos and trichlorfon, as templates for the synthesis of a unique MIP [102].

A SPE sorbent specific to two different groups was also proposed by preparing a dual-layer cartridge containing both a MIP prepared with dimethoate as template (in synthesis conditions previously reported by Martins et al. [58]) and a MIP prepared using terbuthylazine as template for the simultaneous determination of both targets in olive oil samples [107].

As illustrated by studies reported in Table 2, MIPs were applied to the selective extraction of OPPs from different matrices such as water samples, aqueous or hydro-organic extracts of vegetables or of soil. They were also applied to the selective extraction of olive oil by Bakas et al. that mentioned the necessity to dilute the oil sample in hexane to favor the retention of the target analytes while decreasing matrix effects [65,71,81]. To demonstrate the potential of the MIPs in terms of selectivity, chromatograms resulting from the use of the MIPs were compared to chromatograms resulting from liquid-liquid extraction or an extraction on a conventional C18 silica sorbent [70,73,81,102]. In all cases, the chromatograms showed that the MIPs removed compounds that co-extracted with OPPs when using non selective approaches. Two studies also compared the recovery rate on MIP and NIP applied to the same sample: the higher recovery rates obtained on MIP than on NIP confirm the real contribution of the specific cavities in the extraction process of the target analyte of fruit and oil samples [71,97].

4-2- Other extraction methods

Instead of introducing MIP particles between frits in a cartridge, MIP particles can be dispersed in a liquid sample to be put in contact with the target analytes for a suitable time. To obtain well defined particles, authors proposed to replace the polymerization in bulk by precipitation polymerization [59], polymerization on silica particles [39,41] or on iron (II,III) oxide (Fe_3O_4) magnetic nanoparticles [52,91], the magnetic properties of the MIP particles greatly facilitating the development of extraction procedure as recently reviewed [108]. For the extraction of OPPs with this non-exhaustive dSPE method, MIP beads were incubated for 20 min and 2 hours in the sample to favor the binding of the target analytes. After this time that often corresponds to the equilibrium time required for the binding of the target, the beads are separated from the sample by centrifugation [59], by filtration on a membrane [39,41] or by a simple magnetic field when magnetic nanoparticles are used [52,91]. Beads are then put in contact with a washing solvent to improve the selectivity. The desorption of the target is further ensured by introducing the beads in a solvent that disrupts the MIP-target compounds interactions during an incubation time that must be again optimized.

This dispersive method was applied to the extraction of OPPs from soil [52,91] and vegetable [41,52,59] extracts or water samples [39]. As an example, **Fig. 3** shows the application of a MIP-dSPE to the extraction of chlorpyrifos from different vegetables [41]. For this, a MIP was polymerized at the surface of silica nanoparticles (NPs) and 20 mg of these NPs were introduced, dispersed in 5 mL of a chloroform extract of vegetable samples. After incubating for 30 min, NPs were recovered by a filtration through a 0.22 μm membrane to be washed with chloroform. Desorption of chlorpyrifos was achieved in 1h in acidified methanol. Despite this time-consuming procedure, a very high selectivity was obtained as illustrated by the comparison of the chromatograms corresponding to the use of MIP NPs to the direct injection

of the same extract. The selectivity is also demonstrated by the absence of peak of chlorpyrifos when using non imprinted NPs.

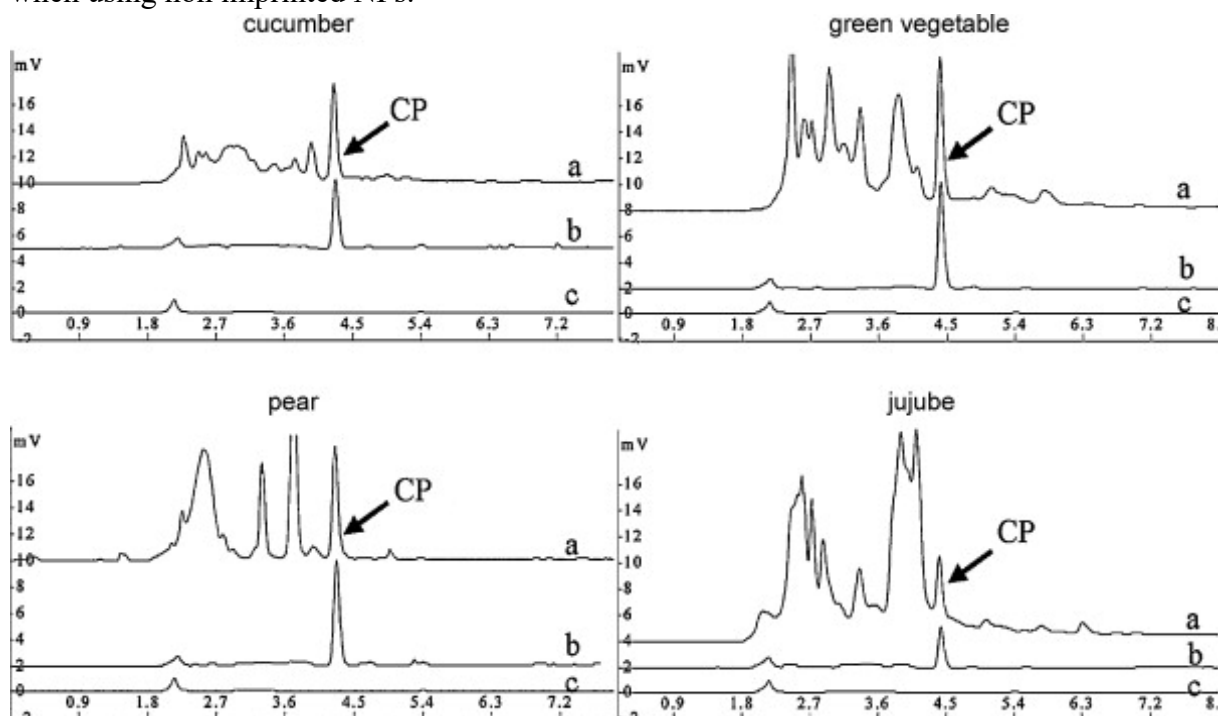


Fig. 3 : HPLC chromatograms of (a) spiked sample solution containing $1 \mu\text{g mL}^{-1}$ chlorpyrifos (CP), (b) spiked sample solution extracted with CP-imprinted nanoparticles, and (c) spiked sample solution extracted with non imprinted nanoparticles [41].

In a similar manner, MIP particles can be dispersed directly in solid matrices to develop a selective matrix solid-phase dispersion (MSPD) method [60,74,98], the MIP replacing conventional sorbents such as silica, bonded silica (C18), Florisil... In this method, forces are applied to the sample by mechanical blending with the sorbent to produce complete sample disruption and the interactions of the sample matrix with this sorbent. The blended material is then transferred and packed into a cartridge suitable for conducting sequential elution with solvents [109]. This approach was used for the extraction of nine OPPs from fruit samples using a MIP produced by dummy approach using 4-(dimethoxyphosphorothioylamino) butanoic acid as template. In their work, authors focused more on finding conditions that favor the recoveries for the nine compounds than on the real selectivity brought by the MIP, the NIP being not studied in parallel in MSPD experiments [60]. To shorten the extraction time and solvent consumption, it was also proposed to combine MSPD with accelerated solvent extraction by submitting the blended material, introduced in a stainless-steel extraction cell, to a pressurized hot organic solvent for the desorption of the target analytes [74].

Other non-exhaustive but nonetheless quantitative methods also based on the equilibrium of the target analyte(s) between small amount of sorbent and the sample such as micro-solid phase extraction (SPME) [43,54,92] or stir-bar sorptive extraction (SBSE) using a MIP as sorbent were proposed for the extraction of OPPs [78].

For SBSE, the stir bar was coated by an imprinted Nylon-6 film imprinted with monocrotophos prepared by phase inversion method [78]. For SPME, the fiber coating was achieved by immersing an activated silica fiber in a sol-gel solution [54,92], the thickness of the MIP layer being defined by the immersion time. A MIP fiber was also prepared by introducing the polymerization mixture in a capillary used as a mold [43].

One of this MIP fiber was prepared by sol-gel approach using methyl parathion as template and calixarene as functional monomer. As shown in **Fig. 4**, the three home-made fibers (MIP, NIP and a blank fiber (synthesized without introducing calixarene)) displayed much better extraction ability than those of the commercial fibers. The positive effect of calixarene on the recognition properties was also proven by the better performance of MIP and NIP-coated fibers compared to blank fiber. This was explained by the contribution of π - π interactions, hydrophobic interactions and inclusion interactions provided by calixarene to enhance the affinity between the fiber and the studied OPPs [92].

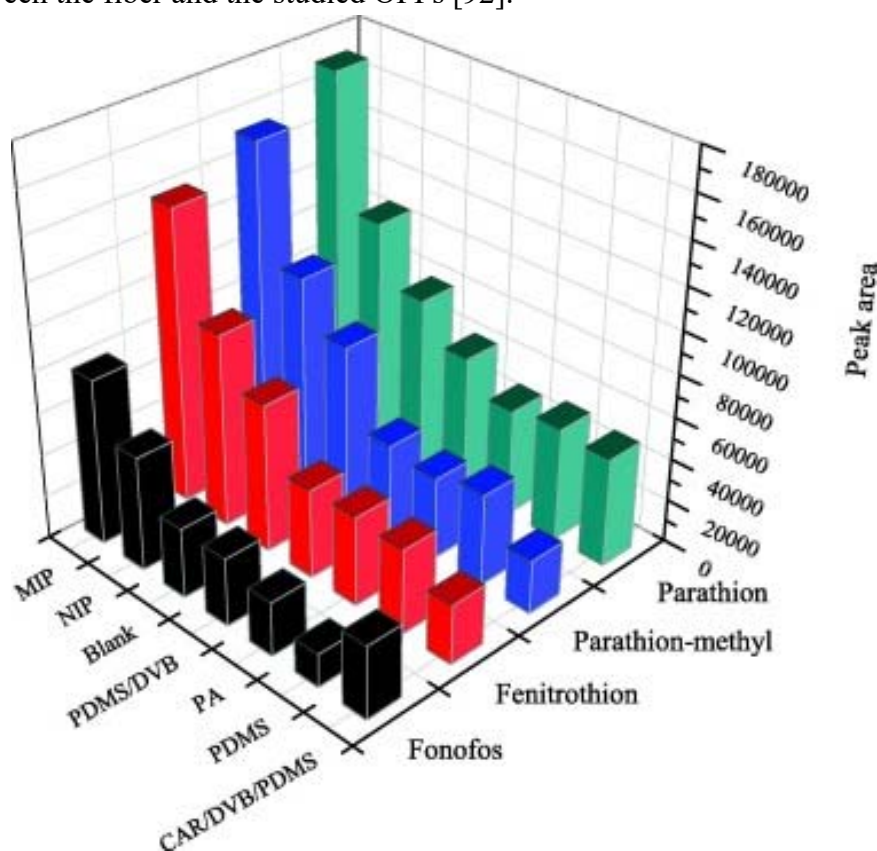


Fig. 4: Extraction capability of the prepared fibers and the commercial fibers (polydimethylsiloxane (PDMS), polyacrylate (PA), PDMS/DVB and Carbowax (CAR)/DVB/PDMS) in spiked water samples [92].

This fiber was applied to the extraction of OPPs from different fruits by diluting 2 g of fruit with 2 ml of water and by extracting the OPPs by introducing the fiber in the head-space of the vial. After 30 minutes, the fiber was introduced in the injector of the gas chromatograph for the thermal-desorption of the OPPs at 250°C. The selectivity brought by the MIP is illustrated by the chromatograms reported on **Fig. 5** that show that the MIP fiber presents higher extraction capabilities than the NIP fiber when applied to pineapple sample [92]. To ensure that the temperature applied for the thermal-desorption of the OPPs from the fiber will not damage the

fibers, some authors made thermo-gravimetric analysis of the synthesized polymer showing that a methacrylic MIP supports a temperature up to 400°C [43] while a MIP prepared by sol-gel was thermostable up to 350°C [54].

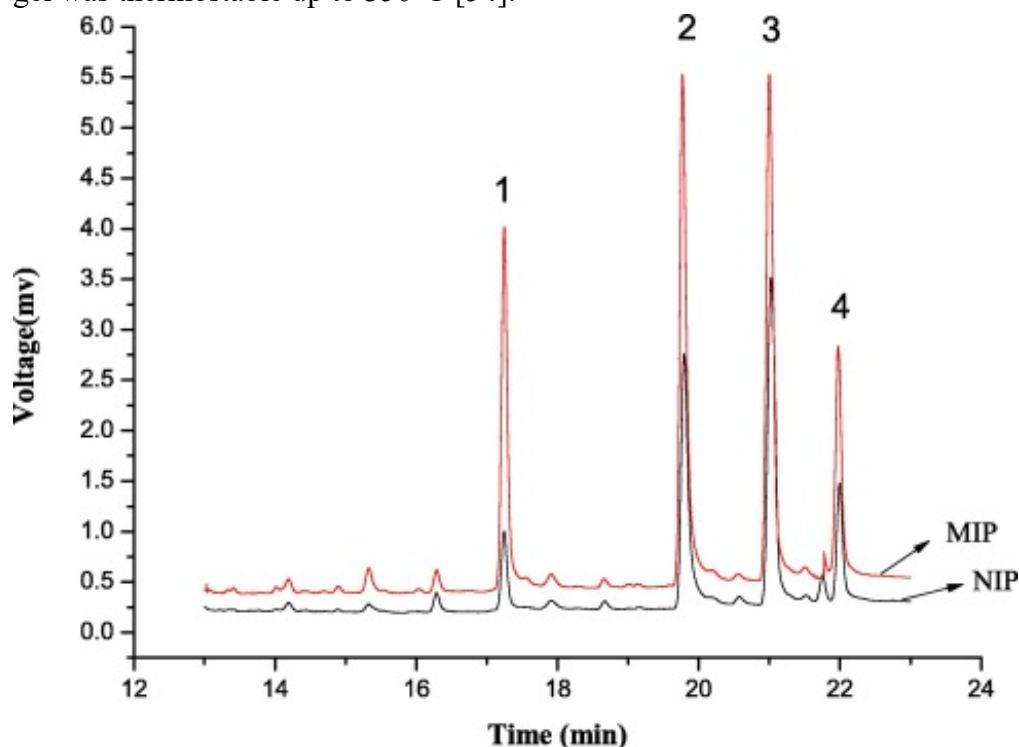


Fig. 5. HS-SPME/GC chromatograms of the spiked pineapple samples. Peaks and spiking levels: 1, fonofos, $10 \mu\text{g kg}^{-1}$; 2, parathion-methyl, $100 \mu\text{g kg}^{-1}$; 3, fenitrothion, $60 \mu\text{g kg}^{-1}$; 4, parathion, $30 \mu\text{g kg}^{-1}$ [92].

Among the studied parameters that affect the recovery rate on the fibers, there are the extraction time, extraction temperature [43,92], pH of the sample for methacrylate based MIP [43] and the salt content of the sample [92].

5. MIP used as sensors

The development of sensors to detect OPPs constitutes an important field of research as reported by Hassani *et al.* in a review dedicated to the development of biosensors for these pesticides in the environment [110]. This recent review only focused on biological tools as sensing elements of recognition (antibodies, aptamers, enzymes, cells). However, Figure 1 shows that the use of MIPs as recognition elements for the development of sensors represents one third of the applications of MIPs for OPPs. Moreover, as recently reviewed, the introduction of MIP in the development of sensors constitutes today a very active research field for a broad range of target molecules [111–114]. For this field of application, the major attracting feature of MIPs is their high stability in real media: they can operate in acid or alkaline conditions, at high temperature in aqueous or organic media... Different types of sensors were developed for OPPs such as piezoelectric sensors (QCM, SPR), optical sensors (fluorescence) and

electrochemical sensors that are the most reported sensors as illustrated by the works summarized in **Table 4**.

One case excepted, the molecule chosen as template for sensor developments was the target molecule that has to be detected in samples when applying the sensor [40,42,44–47,53,66,82,83,85–90,93–96]. In a unique case, DMPTABA was used as template to develop a sensor able to determine the presence of two compounds, acephate and trichlorfon by the same sensor [63].

The development of MIPs for SPE mainly consists in the preparation of MIP as particles (mainly by grinding a monolith obtained by bulk polymerization or by precipitation polymerization). Concerning sensors, in 80% of the cases, MIPs were prepared as a film at the surface of activated NPs, of QDs, of chips, of fibers or on electrodes depending on the type of developed sensors. This film was produced by different methods such as dip-coating, spin-coating, electropolymerization... Nevertheless, MIP particles were mainly involved in electrochemical sensors through immobilizing them on the electrode with the help of a binder. Recently, Gao et al. compared the potential of a sensor developed using MIP particles spin-coated on a QCM electrode or a thin film of MIP produced by *in-situ* self-assembly at the surface of a gold electrode [94]. They showed that the film-based sensor revealed better performances. Indeed, the interface adhesion between the MIP particles and the transducer surface can be poor and the response time can be extremely long due to a because of low mass transfer. Recently, an electrochemical sensor was developed by mixing MIP particles with graphite powder to prepare carbon paste electrode, showing that nanoparticles were better suited than micro particles to develop a highly sensitive electrochemical sensor [53].

Whatever the types of sensor, the film thickness controls the performance of the final sensor. It has been shown that, in the development of electrochemical sensors, a too thick layer gives rise to insulation phenomenon [82]. For these types of sensor, the electropolymerization gains in popularity, certainly owing to the easiest control of the thickness of the MIP film using this approach [114].

As regards QM sensors, the quantification of an OPP was done directly in gas phase [86] or in real water sample extracts after a previous liquid-liquid extraction [94]. For water sample extracts, the quantification was performed by measuring the frequency shift that can be directly correlated with the logarithm of the concentration of profenofos in the liquid sample. The MIP film being prepared at the surface of an electrode, cyclic voltammetry (CV) was first used to evaluate the presence of cavities by comparing the imprinted film to a non imprinted one [94]. As for SPR sensors, the quantification of the OPPs was achieved by measuring the angle or the wavelength shift caused by the bounding of the target OPP that is again proportional to the logarithm of the concentration of the target OPP. For a sensor developed for profenofos by dip-coating a MIP film on an optical fiber, a limit of quantification (LOQ) of $2 \times 10^{-2} \mu\text{g L}^{-1}$ was reported for tap water [95]. To optimize the sensitivity of this sensor, the authors have studied the effect of the amount of template to be introduced during the preparation of the probe on the sensitivity of the sensors.

Regarding the optical sensors for OPPs, the quenching of QD fluorescence when the MIP layer binds chlorpyrifos [44] or the enhancement of the luminescence intensity of the europium-OPP complex [47] was used to quantify the bound amount of OPP.

Most of the electrochemical sensors were based on the measurement of the current resulting from the reduction of the nitro group of some OPPs such as parathion [82,83,85,90], parathion methyl [90,93] and diazinon [53], the measured current being proportional to the amount of OPPs trapped by the MIP. When OPPs cannot be reduced, the sensors were based on the reduction of hexaferrocyanate that is affected by the OPP binding on the MIP film that alters the electron transfer through the film [63,66,88,89]. With these electrochemical sensors, the measure of the signal can be achieved by different methods such as cyclic voltammetry (CV), linear stripping sweep voltammetry (LSSV), square wave voltammetry (SWV) and differential pulse voltammetry (DPV).

To enhance the selectivity, a washing step with water was introduced between the incubation of the sensors with the sample and the measurement of the amount of OPP bound to the MIP [66,85,88,93–95]. This washing was optimized by Alizadeh showing that a washing for 15 s in a water/acetonitrile (98/2) mixture allows the signal on the NIP to be decreased while maintaining the same signal level on the MIP thus improving the selectivity of the response [84].

The potential of sensors is usually given by the linearity range and the limit of detection that can be reached for pure sample and its selectivity towards the target OPP. Most of the developed sensors were selective towards the target OPP with a low ability to recognize other OPPs. An illustration of this selectivity is given by **Fig. 6** that shows the signal obtained for profenofos and 4 other OPPs using an SPR sensor developed for profenofos and by comparing the signal obtained with the MIP-film versus that with NIP-film [96].

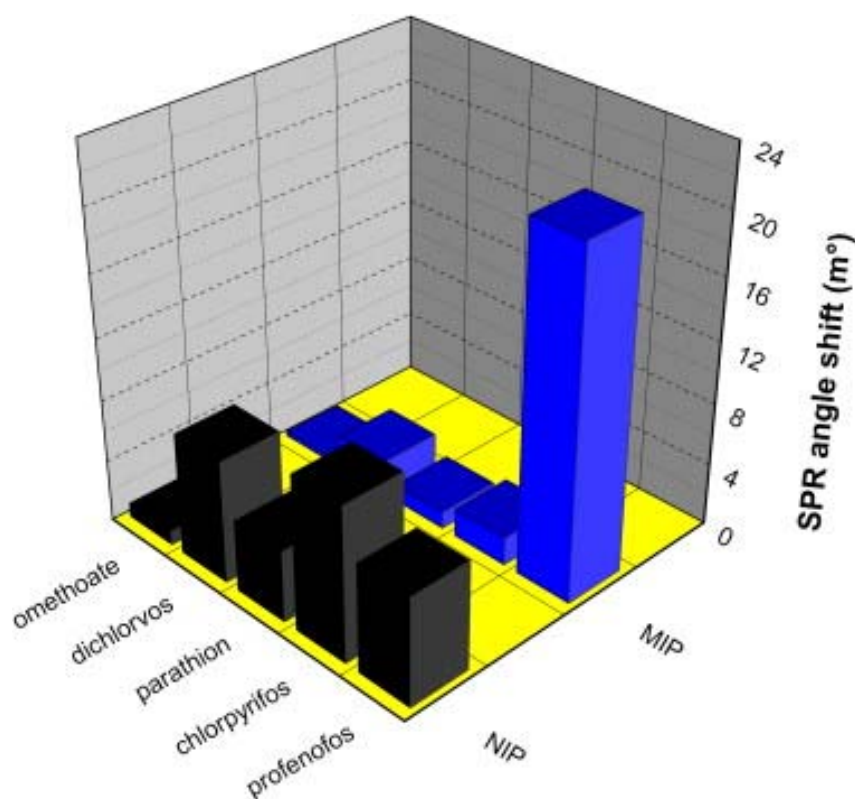


Fig. 6: Selectivity of the profenofos SPR-MIP sensor towards the target OPP and four structural analogs. Sample concentrations were 1 and 10 $\mu\text{g mL}^{-1}$ for MIP and NIP, respectively [96].

Using the MIP-film, the responses of the analogs were significantly lower than those of profenofos. In return, the responses of the five compounds using the NIP-film are similar. These results indicate that the MIP-film has cavities that are complementary only to profenofos in shape, size, and function. The absence of cavities on the NIP film gives rise to non-specific absorption that is similar for the five studied compounds and of relatively low strength, the sample being tenfold more concentrated for experiments on NIP than on MIP.

This selectivity can be improved for electrochemical sensors based on the reduction of nitro group because the measured signal cannot be affected by compounds that cannot be reduced in the same conditions. Among the studied parameters to enhance the sensitivity and the selectivity of the sensor response, there is the pH value of the sample when MAA was used as monomer [40,53,82,86,94–96]. The incubation time is also generally studied to optimize the signal. As shown by incubation times reported in Table 4, the latter varies from 3 min to 10 min for half of the applications but it can reach 12 h. These sensors were rarely applied directly to real samples. Only a few studies reported the direct application of the MIP sensors to real water samples with limits of detection (LOD) ranging 8-17 $\mu\text{g L}^{-1}$ (34-50 nM) [44,88,89]. To reach low concentration level in water samples, a previous liquid-liquid extraction step was introduced to concentrate and transfer the target OPP in an adapted buffer [94,96]. Regarding vegetables, OPPs were previously extracted by water or an aqueous buffer [40,42,63,85] or an organic solvent [45,46] that can be further diluted with water or an appropriate buffer [66,82,87,90,93].

The repeatability of the preparation of the sensors was demonstrated by preparing 5 different electrodes for a sensor developed for methyl parathion with a RSD value of only 6.4% on the signal. Moreover, this sensor showed the same performances after one month storage [90]. For other electrochemical sensors developed for the same target but prepared by another approach (electropolymerization instead of precipitation polymerization), the stability was ensured for 10 days but a loss of 43% of the signal was observed after 1 month [87]. The repeatability of the synthesis of a sensor for isocarbophos prepared by electropolymerization was also demonstrated by 6 independent preparations and their stability was demonstrated over 30 days [66]. Similar results were obtained for sensors developed for acephate and trichlorfon [63] and for chlorpyrifos [45]. In addition to the study of the stability of the sensor during storage, some authors reported the possibility to re-use them more than 5 [95], 6 [96], 30 [85], 50 [45] up to 200 times [42].

6. Miscellaneous applications

Some OPP MIPs were also prepared to be used as stationary phases in HPLC or in electrochromatography. Indeed, to obtain homogeneous particles, MIP particles were prepared by precipitation polymerization and packed in a 150 x 4.6 mm I.D. column to be applied to the separation of several OPPs [49]. The high efficiency that can be expected when using electrokinetic separation methods was exploited by Zhao et al who prepared organic-inorganic hybrid monolithic column by in-situ synthesis of the polymer in a 35 cm x 100 μm I.D. capillary. This capillary was applied to the analysis of trichlorfon in cucumber and cauliflower extracts by electrochromatography [100].

A MIP for trichlorfon was also prepared by bulk polymerization using MAA, EGDMA in chloroform and the resulting particles were used to replace antibodies in an immunoassay-capillary electrophoresis method [101]. As for a conventional immunoassay, an enzyme conjugate was prepared by linking the pesticide to horse radish peroxidase (HRP). A competition between the OPP and its conjugate for the MIP takes place and after the removal of the supernatant, MIP particles were eluted to inject trichlorfon in capillary electrophoresis for its analysis. The ability of the MIP to recognize other OPPs was measured and low cross-reactivity values of 16% and 13.3% were obtained for monocrotophos and omethoate, respectively, in this competitive context. A LOD of $0.13 \mu\text{g L}^{-1}$ was obtained in pure media. This method was further applied to vegetable extracts.

7. Conclusions

This review demonstrates that the predetermined recognition ability of MIPs for a target OPP, their stability, relative ease and low cost preparation in under various formats (particles, membrane, film...) make them very attractive for being used as alternatives to biological entities, such as antibodies, for the development of extraction devices and sensors. Although most of the development of MIPs has been carried out in the biological and the clinical fields, their potential as selective tools in analytical techniques dedicated to the environmental domain and food survey is particularly well-illustrated by the numerous developments related to the analysis of OPPs.

Their use in extraction devices certainly remains the most active area but the increasing development in the field of sensors highlights the high potential of MIP for targeted analysis. Indeed, the large range of physico-chemical properties of OPPs renders difficult the design of adequate conditions of synthesis of a MIP able to trap a large number of molecules of this class of pesticides as it was demonstrated for other classes of pesticides such as triazine herbicides.

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Table 1: Conditions of synthesis of MIPs for the recognition of OPPs. Underlined reagents correspond to reagents that were finally selected in the studies.

Template	Synthesis	M/CL	Solvent	Initiation	Ref
Acephate	Bulk	MAA/ EGDMA	CHCl ₃ : H ₂ O (8:3)	AIBN /58°C	[38]
	Pickering emulsion	MAA /EGDMA	CHCl ₃		[39]
	Surface grafting on Au	MAA/ TRIM	CH ₃ CN	ABAH/ UV	[40]
Chlorpyrifos	Polymerization on silica NPs	MAA/ EGDMA	CH ₃ CN / Toluene 3/1	BPO/50 to 85°C	[41]
	Polymerization on silica particles	AA/ EGDMA	CH ₃ CN	AIBN	[42]
	Bulk	MAA/ EGDMA	CH ₃ CN / MeOH 2/1	AIBN /60°C	[43]
	Polymerization on QD	AAM/ EGDMA	EtOH	AIBN /60°C	[44]
	Electropolymerization on NP	PD	-	-	[45]
	Polymerization on NP	dopamine	-	-	[46]
Chlorpyrifos methyl, diazinon	Polymerization on a fiber	vinylbenzoate + Europium/styrene+DVB	Water/ MeOH	AIBN /60°C	[47]
D4DNP	Precipitation	imidazole + Co ⁺ /DVB	CH ₃ CN	AIBN /60°C	[48]
DEP	Precipitation	MAA, IA, AAM /EGDMA	CHCl ₃	60°C	[49]
DETP	Bulk	4-VP/ EGDMA	CH ₃ CN	AIBN /65°C	[50]

Diazinon	Bulk	MAA/ EGDMA	CHCl ₃	AIBN /60°C	[51]
	Dispersion	MAA+HEMA /EGDMA	MeOH / CH ₃ CN 1/4	AIBN /60°C	[52]
	Precipitation and suspension	MAA/ EGDMA	CHCl ₃	AIBN /60°C	[53]
	Sol-gel coating	PEG /TEOS, PMHS	Toluene		[54]
Dichlorvos	Bulk	MAA / TRIM	CH ₃ CN	AIBN	[55]
Dimethoate	Bulk	BMA, MMA, EMA / EGDMA	THF	AIBN /60°C	[56]
	Membrane coating	MAA,AA/ polyacrylonitrile/ N-methylpyrrolidone	-	-	[57]
	Living radical	MAA/ EGDMA	CH ₃ CN	AIBN, TED /UV	[58]
	Precipitation	MMA, MAA, AAM/ EGDMA	CH ₃ CN	AIBN /20°C	[59]
DMPTABA	Bulk	AAM/ EGDMA	CH ₃ CN	AIBN /60°C	[60,61]
	Film produced at the surface of 96-well plate	MAA/ EGDMA	-	AIBN	[62]
	Sol-gel	APTES/ TEOS	-	ammonia	[63]
Fenitrothion	Bulk	MAA/ EGDMA	CH ₂ Cl ₂	AIBN /65°C	[64]
Fenthion	Bulk	AAM/ EGDMA	DMF	AIBN	[65]
Isocarbophos	Electropolymerization	PD/GA/ABA	-	-	[66]

Malathion	Precipitation	MAA/ EGDMA	CH ₃ CN / CHCl ₃	AIBN /70°C	[67]
		MAA+GMA /EGDMA	CHCl ₃		[68]
Methamidophos	Bulk	MAA/ EGDMA	CH ₂ Cl ₂	AIBN /58°C	[69,70]
Methidation	Bulk	MBAA ,IA, MAA, TFMAA/ EGDMA	DMF	AIBN /80°C	[71]
Monocrotophos	Bulk	MAA/ EGDMA	CH ₂ Cl ₂	AIBN /58°C	[72– 74]
			-	-	[75]
			CHCl ₃	AIBN /58°C	[76]
	nylon membrane	MAA, AA, AAM /EGDMA	Toluene, CH ₃ CN, CH ₂ Cl ₂	AIBN /65°C	[77]
	Phase inversion/Nylon-6	Nylon-6	-	-	[78]
	Precipitation	MAA/ EGDMA	Toluene	AIBN /60°C	[79]
O,O-dimethyl thiophosphoryl chloride (dummy)	Bulk	MAA/ EGDMA	CHCl ₃	AIBN /58°C	[80]
Omethoate, dimethoate, monocrotophos	Bulk	IA, MAA, TFMAA/ EGDMA	DMF	AIBN /80°C	[81]
Parathion	Bulk	MAA/ DVB	EtOH	AIBN /60°C	[82]

	silica gel grafting	PEI /EGDMA	basic solution		[83]
	Precipitation	MAA/ EGDMA	CHCl ₃	AIBN /60°C	[84]
	Sol-gel film (spin-coating)	p-tert-butylcalix[6]arene /PMHS, TEOS, OH-TSO -1,4-crown-4	CH ₂ Cl ₂ / EtOH	TFA	[85]
Parathion or paraoxon	Sol-gel film (spin-coating)	PTMOS, APTES/ TEOS	EtOH	HCl	[86]
Parathion methyl	Electropolymerization	aminothiophenol	-	-	[87]
	Electropolymerization	quercetin, resorcinol, dodecanethiol	-	-	[88]
	Electropolymerization	phenol	-	-	[89]
	Precipitation	MAA /EGDMA	MeOH	AIBN /60°C	[90]
	Polymerization on NP	MAA :4-VP/ EGDMA	CHCl ₃	AIBN	[91]
	Sol-gel	calix[4]arene /PMHS, TEOS, OH-TSO	CH ₂ Cl ₂	TFA	[92]
Parathion methyl /parathion/paraoxon	polymerization on MWCNTs	AAM/ EGDMA	CH ₃ CN / Toluene/ DMF (15/2/3)	AIBN /70°C	[93]
Profenofos	precipitation and spin-coating/in situ self assembly on Au electrode	MAA/ EGDMA or TRIM	CH ₃ CN / DMSO	AIBN, ABAH /60°C	[94]
	coating of Ag film	MAA/ TRIM	DMSO		[95]
	polymerization on Au chip	MAA/ TRIM	DMSO	ABAH /60°C	[96]

Quinalphos	Bulk	MAA/ EGDMA	CH ₃ CN	AIBN /60°C	[97]
Tolchlofos-methyl (dummy)	dispersion polymerization with γ -MAPS activated silica NP	MAA/ EGDMA	CH ₃ CN	AIBN /60°C	[98]
Trichlorfon	Bulk	MAA/ EGDMA	CHCl ₃	AIBN /60°C	[99]
	in-situ polymerization into a capillary	MAA / γ -MAPS	MeOH / toluene 3/2	AIBN /50°C	[100]
	Bulk	MAA/EGDMA	CHCl ₃	AIBN/58°C	[101]
Trichlorfon + monocrotophos	Bulk	MAA/ EGDMA	CHCl ₃	AIBN /58°C	[102]

4-VP: 4-vinylpyridine, AA: acrylic acid ; AAM: acylamide; ABA: m-aminobenzoic acid ; ABAH: 2,2'-Azobis (2-amidino propane) hydrochloride; AIBN : 2,2-Azobis-(2-methylpropionitrile); APTES: aminopropyl triethoxysilane; BMA: butylmethacrylate ; CHCl₃: chlorofom; CH₂Cl₂: dichloromethane; CH₃CN: acetonitrile; CL : cross-linker ; BPO : benzoyl peroxide ; D4DNP: diethyl(4-nitrobenzyl)phosphonate ; DMPTABA: 4-(dimethoxy phosphorothioylamino)butanoic acid; DCM: dichloromethane ; DEP : diethyl(3-methyl ureido)(phenyl)methylphosphonate ; DETP: diethylthiophosphate; DMF: dimethylformamide; DMSO: dimethylsulfoxide ; DVB : divinylbenzene ; EGDMA; ethyleneglycoldimethacrylate; EMA: ethyl methacrylate; EtOH : ethanol ; GA : gallic acid ; GDMA: glycerol dimethacrylate; GMA: glycidimethacrylate; HEMA: 2-hydroxyethyl methacrylate ; IA: itaconic acid; M : monomer ; MAA: methacrylic acid; MBAA : N,N'-Methylenebisacrylamide MMA: methyl methacrylate ; MeOH: methanol; MWCNT: multiwall carbon nanotube NP : nanoparticles ; OH-TSO: hydroxy terminated silicone oil ; PEG: polyethylene glycol; PEI: polyethyleneimine ; PMHS: poly (methylhydrosiloxane); PTMOS: phenyltrimethoxysilane; QD : quantum dots ; TED: tetraethyl thiuram disulfide; TEOS: tetraethyl orthosilicate ; TFA: trifluoroacetic acid ; TFMAA: trifluoromethylacrylic acid ; THF: tetrahydrofuran; TRIM: trimethylol propane trimethacrylate ; γ -MAPS: γ -methacryloxypropyl trimethoxysilane ; PD : o-phenylenediamine

Table 2: MIPs involved in extraction methods. Underlined compounds correspond to are those studied in real samples, compounds in bold are those whose selectivity was proven by a comparative study on NIP as control SPE sorbent (not only by binding experiments).

Use	Template	synthesis	Monomer / CL/ Porogen	Matrix	Studied compounds	Ref
SPE	chlorpyrifos	Dispersion/ silica particles	AA / EGDMA /ACN	spinage	<u>chlorpyrifos</u> , methyl-parathion, parathion	[42]
	DETP	Bulk	4-VP /EGDMA /ACN	urine	<u>DETP, DEDTP</u>	[50]
	diazinon	Bulk	MAA /EGDMA /CHCl ₃	cucumber	<u>diazinon</u>	[51]
	dichlorvos	Bulk	MAA/TRIM /ACN	Water, vegetables	<u>Dichlorvos</u> , phoxim, chlorpyrifos	[55]
	dimethoate	Living radical polymerization	MAA/ EGDMA/ACN	olive olive oil	<u>dimethoate</u> , omethoate, malathion, fenthion methidation	[58]
	DMPTABA	Bulk	AAM /EGDMA/ ACN	cucumber	<u>dimethoate, isocarbophos, methyl-parathion</u>	[61]
	fenitrothion	Bulk	MAA/EGDMA /CH ₂ Cl ₂	tomato	<u>fenitrothion</u>	[64]
	fenthion	Bulk	AAM/ EGDMA /DMF	olive oil	<u>fenthion, fenthion sulfoxide</u> , dimethoate, methidathion, malathion	[65]
	malathion	Precipitation	MAA /EGDMA ACN : CHCl ₃ 1 : 1	tap water, soil, cabbage	<u>malathion</u> , malaaxon, profenofos, triazophos	[67]
			MAA :GMA /EGDMA CHCl ₃	Honey	<u>malathion, ethophos, phorate, terbuphos, dimethoate, fenamiphos</u>	[68]
methamidophos	Bulk	MAA/EGDMA /CH ₂ Cl ₂	surface water, soil	<u>methamidophos</u> , acephate, monocrotophos, phosphamidon	[70]	

	methidation	Bulk	MBAA/ EGDMA / DMF	olive oil	methidation , dimethoate, malathion, fenthion	[71]
	monocrotophos	Bulk	MAA/EGDMA /CH ₂ Cl ₂	river and tap water, soil	<u>monocrotophos</u> , mevinphos, phosphamidon, omethoate	[73]
MAA /EGDMA/ CHCl ₃			Rape, cauliflower, leek	monocrotophos	[76]	
Polymerization/ nylon membrane		MAA/ EGDMA/ Toluene	pure water	monocrotophos , mevinphos, phosphamidon, omethoate	[77]	
	O,O-dimethyl thiophosphoryl chloride	Bulk	MAA/ EGDMA/ CHCl ₃	water, vegetables	<u>dichlorvos, methamidophos, acephate, folimat, monocrotophos, methyl-parathion, phosphamidon, malathion</u>	[80]
	omethoate	Bulk	IA / EGDMA/ DMF	olive oil	omethoate, dimethoate , methidation, monocrotophos, malathion, fenthion	[81]
	quinalphos	Bulk	MAA / EGDMA / ACN	fruit	 diazinon, quinalphos, chlorpyriphos	[97]
	trichlorfon	Bulk	MAA /EGDMA/ CHCl ₃	vegetables	<u>trichlorfon</u> , omethoate, acephate	[99]
	trichlorfon + monocrotophos	Bulk	MAA /EGDMA/ CHCl ₃	leek	<u>trichlorfon, monocrotophos, methamidophos, acephate</u>	[102]
dSPE	acephate	pickering emulsion / SiO ₂ NP	MAA /EGDMA/ CHCl ₃	waters	<u>acephate</u> , methamidophos, isocarbophos and malathion.	[39]
	chlorpyrifos	Dispersion/ silica NPs	MAA /EGDMA /ACN : Toluene 3 :1	green vegetable	<u>chlorpyriphos, profenofos, ltriazophos, phoxim</u>	[41]

	diazinon	dispersion / Fe ₃ O ₄ NP (magnetic)	MAA :HEMA /EGDMA / MeOH: ACN 1:4	soil, cucumber	diazinon	[52]
	dimethoate	Precipitation	MAA / EGDMA / ACN	cucumber	<u>dimethoate</u> , methamisophos, carbaryl	[59]
	methyl-parathion	polymerization / Fe ₃ O ₄ NP (magnetic)	MAA :VP /EGDMA/ CHCl ₃	soil	<u>methyl-parathion</u> , malathion, methamidophos	[91]
MSPD	DMPTABA	Bulk	AAM / EGDMA / ACN	apple, pear	<u>trichlorfon, malathion, acephate, methamidophos, omethoate, dimethoate, phosphamidon, monocrotophos, methyl parathion</u>	[60]
	monocrotophos	Bulk	MAA/EGDMA /CH ₂ Cl ₂	soil	<u>monocrotophos</u> , fenitrothion, parathion, fenthion, phoxim	[74]
	tolclofos-methyl (dummy)	dispersion / γ -MAPS activated silica NP	MAA / EGDMA / ACN	Carrot, Yacon	<u>tolclofos methyl, methyl-parathion, chlorpyrifos, phoxim, iprobenphos</u>	[98]
SBSE	monocrotophos	Phase inversion/ Nylon-6	Nylon-6	soil	Monocrotophos	[78]
SPME	chlorpyriphos	Bulk	MAA/EGDMA /ACN :MeOH 2 :1	Apple, grapes	<u>chlorpyriphos</u> , diazinon, malathion, parathion	[43]
	diazinon	Sol-gel coating	PEG /TEOS, PMHS /Toluene	Water, vegetable	<u>methyl-parathion, diazinon, pirimiphos-methyl, isocarbophos</u>	[54]
	methyl-parathion	Sol-gel	calix[4]arene/PMHS, TEOS, OH-TSO/CH ₂ Cl ₂	fruits	<u>methyl-parathion</u> , parathion, fenitrothion, fonofos, fenthion	[92]

Table 3: Recovery rates (%) of 5 OPPs loaded as 5-mL aliquots of 1 mg L⁻¹ solution onto acrylamide-based MIP and corresponding NIP. The calculations are based on triplicates, the RSD values are below 5% [65].

Analytes	MIP		NIP	
	Washing	Elution	Washing	Elution
Fenthion	4 ± 3.2	97 ± 4.1	95 ± 4.8	4 ± 2.1
Dimethoate	98 ± 3.7	nd*	97 ± 3.2	nd
Fenthion-sulfoxide	nd	93 ± 3.3	95 ± 4.4	nd
Methidathion	96 ± 3.5	6 ± 3.6	95 ± 3.6	nd
Malathion	97 ± 5	nd	98 ± 4.2	nd

Table 4: MIP used as recognition element in sensors for OPPs

Type of sensor	Measured signal or technique	template	Mode of polymerization	Medium	T	Linear range	LOD	Ref
QCM	frequency shift	Parathion or paraoxon	Dip-coating of a sol-gel film on QCM crystal	gas phase	10 min	-	-	[86]
	frequency shift	Profenfos	in-situ self assembly of MIP film on gold electrode	real water (after LLE)		10^{-8} to 10^{-5} mg mL ⁻¹	0.2 μ g L ⁻¹	[94]
SPR	wavelength shift	acephate	Ultra-thin film anchored on Au slide glass	apple and cole (aqueous extracts)		0.5 to 8 pM	1.14 10^{-13} M (apple), 4.29 10^{-14} M (cole)	[40]
	angle shift	Chlorpyriphos	MIP film on Fe ₃ O ₄ NP surface	apple (ACN extract)	> 12h	0.001-10 μ M	0.76 nM	[46]
	angle shift	profenfos	Ultra-thin film anchored on the surface of an Au-chip	tap water (after LLE)	30 min	0.001 to 0.1 μ g mL ⁻¹	3.6 10^{-4} μ g mL ⁻¹	[96]
	wavelength shift		Dip-coating of a MIP film on Ag film supported by an optical fiber	real waters		10^{-4} to 10^{-1} μ g L ⁻¹	2.5 10^{-6} μ g L ⁻¹ (PBS) ; 2 10^{-4} μ g L ⁻¹ (drinking water) ; 2	[95]

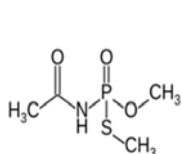
							$10^{-2} \mu\text{g L}^{-1}$ (tap water)	
Fluorescence	quenching of QD fluorescence	chlorpyrifos	MIP film on QD	river water	40 min	0.3 to 60 μM	50 nM	[44]
	effect on Eu^{3+} luminescence	chlorpyrifos methyl, diazinon	MIP film on a fiber optic probe	pure water	15 min	5-7 ppt to 100 ppm	250 ppb	[47]
Electro-chemical	SWV	Diazinon	MIP NPs mixed with graphite powder	well water, apple	10 min	2.5nM to 0.1 μMol	$7,9 \cdot 10^{-10} \text{mol L}^{-1}$	[53]
	DPV, $\text{Fe}(\text{CN})_6^{3-}$	isocarbophos	electropolymerization of a MIP film on GCE	ethanol extracts of vegetable diluted in water	5 min	75 nM to 50 μM	20 nM	[66]
	LSSV	Parathion methyl	electropolymerization of a MIP film on Au-NP modified MWCNT-GCE	ethanol extract of apple and cucumber (concentrated x15 and diluted x50 in buffer), tap water	6 min		0.08 ng mL^{-1}	[87]
	CV, $\text{Fe}(\text{CN})_6^{3-}$		electropolymerization of a MIP film on Au electrode modified by	river water		0.1 to 10 $\mu\text{g mL}^{-1}$	0.01 $\mu\text{g mL}^{-1}$	[89]

			nitrogen-doped graphene sheet					
	impedance, /Fe(CN) ₆ -		electropolymerization of a MIP film on the surface on Au-NP	tap, river, rain waters	280 s	70 nM to 1 μM	34 nM	[88]
	DPV		Film formed with a mix of MIP beads (precipitation), ionic liquid and graphene oxide at the surface of GCE	cabbage and apple peel extract diluted in PBS (x10)	150 s	0.01 to 7 μM	6nM	[90]
	DPV	Parathion	spin-coating of sol-gel film on CGE	phosphate buffer	20 min	5nM to 0.1 mM	≈ 1 nM	[85]
	SWV		MIP particles (obtained by precipitation) incorporated in a CPE	tap water and cabbage sample	10 min	1.7 to 900 nM	0.5 nM	[84]
	CV		MIP particles obtained by silica gel grafting immobilized on GCE using chitosan	cucumber, cabbage (aqueous extracts)	50 min	0.015 to 15 mg kg ⁻¹	3 μg kg ⁻¹	[83]
			Coating of MIP particles on GCE with DPH	pear juice (diluted in buffer)	210 s	0.1 μM to 10 μM	54nM	[82]

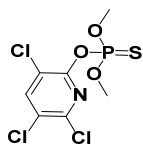
	CV	Parathion or paraoxon	spin-coating of a sol-gel film on activated GCE	phosphate buffer	-	-	-	[86]
	DPV	Me parathion/ parathion/ paraoxon	polymerization of a film at the surface of vinylized MWCNTs	pear, cucumber (extract diluted in a buffer)	3-5 min	0.2 μ M to 10 μ M	60 nM	[93]
	DPV , Fe(CN) ₆ ³⁻	DMPTAB	Electrodeposition of a film of MIP of GCE coated by Fe ₃ O ₄ -MWCNT	kidney bean, cucumber (buffer extract)	20 min	10 ⁻⁴ to 10 ⁻¹⁰ M (acephate); 10 ⁻⁵ to 10 ⁻¹¹ M (trichlorphon)	9-70 pM	[63]
Photoelectrochemical	photocurrent measurements	chlorpyrifos	Electropolymerization of a film on Au-NP-TiO ₂ -NT	vegetable (hexane extraction, methanol addition, dilution x 1000 with buffer)	15 min	0.05 to 10 μ M	0.96 nM	[45]

DPV : differential pulse voltammetry ; GCE : glassy carbon electrode ; CPE : carbon paste electrode ; CV : cyclic voltammetry ; DHP : dihexadecyl hydrogen phosphate; LSSV : linear stripping sweep voltammetry ; NP : nanoparticles ; NT : nanotubes, QD : quantum dots ; SWV : Square wave voltammetry

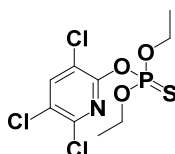
Supplementary material S1 : Structure and log P values of organophosphorus pesticides



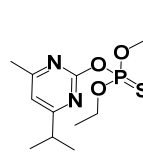
Acephate
log P = -0.85



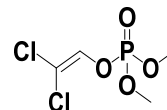
Chlorpyrifos-
methyl



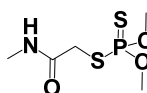
Chlorpyrifos-ethyl
log P = 4.7



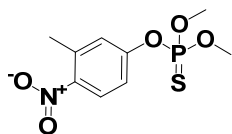
Diazinon
log P = 3.69



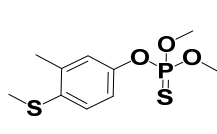
Dichlorvos
log P = 1.9



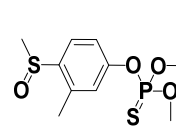
Dimethoate
log P = 0.70



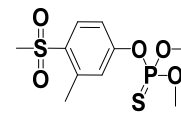
Fenitrothion
log P = 3.32



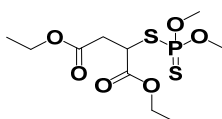
Fenthion
log P = 4.84



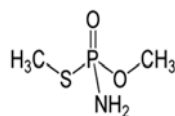
Fenthion sulfoxide
log P = 1.92



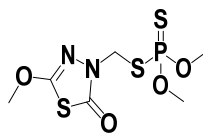
Fenthion sulfone
log P = 2.25



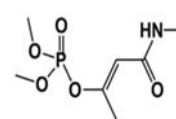
Malathion
log P = 2.75



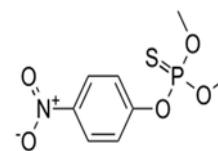
Methamidophos
log P = -0,8



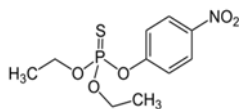
Methidathion
log P = 2.5



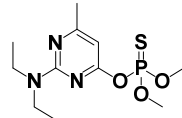
Monocrotophos
log P = 1.05



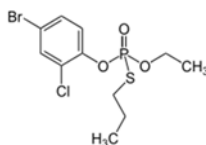
Parathion methyl
log P = 3.2



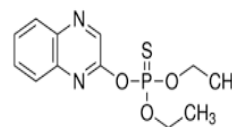
Parathion (ethyl)
log P = 3.8



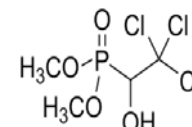
Pirimiphos methyl
log P = 3.9



Profenofos
log P = 4.68



Quinalphos
log P = 4.4



Trichlorfon
log P = 0.48