



# Design and development of molecularly imprinted polymers for the selective extraction of deltamethrin in olive oil: An integrated computational-assisted approach



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## ABSTRACT

This work firstly addresses the design and development of molecularly imprinted systems selective for deltamethrin aiming to provide a suitable sorbent for solid phase (SPE) extraction that will be further used for the implementation of an analytical methodology for the trace analysis of the target pesticide in spiked olive oil samples. To achieve this goal, a preliminary evaluation of the molecular recognition and selectivity of the molecularly imprinted polymers has been performed. In order to investigate the complexity of the mechanistic basis for template selective recognition in these polymeric matrices, the use of a quantum chemical approach has been attempted providing new insights about the mechanisms underlying template recognition, and in particular the crucial role of the crosslinker agent and the solvent used. Thus, DFT calculations corroborate the results obtained by experimental molecular recognition assays enabling one to select the most suitable imprinting system for MISPE extraction technique which encompasses acrylamide as functional monomer and ethylene glycol dimethacrylate as crosslinker. Furthermore, an analytical methodology comprising a sample preparation step based on solid phase extraction has been implemented using this “tailor made” imprinting system as sorbent, for the selective isolation/pre-concentration of deltamethrin from olive oil samples. Molecularly imprinted solid phase extraction (MISPE) methodology was successfully applied for the clean-up of spiked olive oil samples, with recovery rates up to 94%.

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## 1. Introduction

Molecular imprinting technology (MIT) has emerged as a versatile technique widely used for the synthesis of “tailor-made” polymeric materials affording the production of highly cross-linked materials, as stable recognition matrices for a wide range of analytes, mimicking the recognition mechanism of antigens and antibodies. These materials are considered to be artificial receptors possessing highly specific sites towards the target molecule presenting additionally improved properties, namely higher physical robustness, strength, resistance to temperature and pressure as well as stability in acid and basic media [1]. During the imprinting

process, an *in situ* formation of the monomer template complex is considered as a key step followed by the use of a crosslinker entity that allows the preservation of the structure of the monomer template complex and, thus the creation of an artificially generated three-dimensional polymer network which possesses binding sites with structural and functional groups complementary to the template molecule. After the polymerization process, the template molecule is removed from the polymer leaving specific recognition sites complementary in shape, size and chemical functionality to the template molecule, allowing the MIP be able to recognize and bind selectively to only the template molecule. Moreover, the less expensive synthesis and the higher storage stability – keeping their recognition ability for several years at room temperature – and reusability, constitute the major advantages of these imprinting materials [2]. The remarkable properties of these imprinting systems have allowed their widespread application over several fields covering chemistry – chromatography [3,4], catalysis [5,6],

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sample preparation [7]; biology – drug delivery [8] and engineering – sensor technology [9,10].

Over the last years, the use of molecular modelling methods for the study and characterization of MIPs has emerged as a rational design tool that enables one to optimize the MIP formulations and is a promising approach for finding highly selective MIPs [11]. This approach improves the tedious and time-consuming conventional method of MIP synthesis especially if the variation in the formulation is performed by trial-and-error. Some reviews covering the computational aspects of MIP study and design recently appeared in the literature [12–15]. However, the main drawback of the computational approach arises from the difficulty in simulating the real recognition process in MIPs being usually restricted to the rationalization of the interactions between the functional monomers and the template during the pre-polymerization stage [16]. A better stability of a given monomer/template complex in the pre-polymerization stage is typically correlated with a better imprinting effect of the functional monomer towards the template. The porogen is typically treated using continuum solvation models [17], and the cross-linker is mostly ignored. Other rational MIP design computational approaches, including atomistic and coarse-grain molecular dynamics methods that can describe the polymerization itself, or tackle issues such as the template aggregation were also reported [18,19]. Nevertheless, most of the studies found in the literature focus on the pre-polymerization stage [20–22].

Hence, computational modelling have proven to be a helpful guide to the selection of the more appropriate formulations contributing to the development of “rationally designed” selective MIPs for a broad range of templates. Moreover, this approach has also become a powerful tool to elucidate the physical mechanisms underlying the ligand selectivity of the polymeric sorbents prepared by molecular imprinting technology.

In recent years, the use of organochlorides and organophosphorus insecticides has declined owing to their high toxicity being replaced by pyrethroids. Deltamethrin is a synthetic pyrethroid widely used to control insect pests in crops, however, this substance still presents high toxicity affecting the central nervous system of humans and is also suspected to have endocrine-disrupting effects with a long persistence and a high toxicity to the aquatic environment [23]. Thus, the eventual presence, even at trace levels, of this substance in foodstuffs is a matter of great concern making it necessary the development of robust analytical methodologies that enable high precision and selective detection and quantification.

The use of molecular modelling studies to elucidate the molecular interactions within the imprinting system for the development of deltamethrin selective MIPs has never been attempted. In fact, very few reports on deltamethrin-molecularly imprinted polymers in the literature have been described to date [24–27]. Recently, a chemiluminescence nanosensor has been developed based on a quantum dot MIPs – based and used for the selective detection of trace amounts of deltamethrin in fruits and vegetables [28,29].

The propose of this work is the implementation of a highly selective sample preparation methodology based on molecularly imprinted solid phase extraction (MISPE) for the pre-concentration/isolation and further quantification of trace amounts of deltamethrin in olive oil samples. To achieve this goal, the present study addresses the synthesis and chemical characterization of molecularly imprinted polymers selective for deltamethrin by means of chemical and morphological techniques and, furthers the evaluation of the molecular recognition of these imprinting systems. Additionally, computational modelling studies have been used as a tool to understand the molecular imprinting process at the molecular level.

Hence, in this work a molecularly imprinted polymer selective for deltamethrin was successfully used as SPE sorbent for

the implementation of the MISPE methodology allowing the pre-concentration/isolation of deltamethrin and further quantification by HPLC-DAD in spiked olive oil samples. High reproducibility's and recovery rates were observed.

## 2. Experimental

### 2.1. Chemicals

Acrylamide (AM) and metacrylic acid (MAA) (the functional monomers), ethylene glycol dimethacrylate (EGDMA; crosslinker), 1,1'-azobisisobutyronitrile (initiator), were purchased from Sigma–Aldrich, dichloromethane for synthesis and acetic acid and methanol for MIP washing were obtained from Merck. All the chemicals were used as received.

HPLC grade acetonitrile and methanol, n-heptane and dichloromethane were purchased from VWR International S.A.S. (Fontenay-Sons-Bois, France). The water used in all experiments was distilled and purified by a Milli-Q system (Millipore, Bedford, MA, USA). The analytical standards deltamethrin,  $\lambda$ -cyhalothrin, fenpropathrin and phenothrin were purchased from Sigma–Aldrich (Bellefonte, PA, USA) and were used without further purification. The 3 mL reservoir glass columns with their frits were supplied by Chromabond-Macherey-Nagel (Germany). Previously to HPLC injection all samples were filtered through 13 mm syringe filters (w/0.45  $\mu$ m PTFE membrane) (VWR, USA). The organic extra virgin olive oil was purchased from a local supermarket.

### 2.2. Instrumentation

The morphology of the synthesized copolymers were characterized using SEM on a Hitachi S-3700N instrument, with an accelerating voltage set to 10 kV. Samples were mounted on aluminium stubs using carbon tape and were gold coated.

FTIR spectroscopy analysis measurements were performed on a PerkinElmer Spectrum Two IR spectrophotometer.

All the chromatographic measurements were performed using a HPLC Waters Alliance System 2695-series Separation Module equipped with Alliance Series Column Heater and the detection was carried out using a photodiode array detector (2998 PDA Detector) (Waters, USA). Chromatographic experiments were carried out with a LiChroCART C18 Purospher STAR reverse phase column (250 mm  $\times$  4.6 mm ID, 5  $\mu$ m) (Merck Millipore, Germany) and the detection has been performed in the range of 190–600 nm. Empower 3 FR2 software was used for management, acquisition and treatment of data.

### 2.3. Synthesis of the molecular imprinting systems

The synthesis of two different molecular imprinted polymers, MIP1 and MIP2, and their corresponding non-imprinted polymers, NIP1 and NIP2 were carried out using a bulk polymerization method, with the functional monomers MAA (MIP1) and AM (MIP2), respectively, the cross-linker EGDMA, dichloromethane as the porogen and with deltamethrin (template), and in its absence in the case of the non-imprinted polymer (NIPs) (Fig. 1). Briefly, deltamethrin-MIPs were synthesized using a molar ratio of template, radical initiator, functional monomer, and crosslinker of (1:1.9:4:20). To a 50 mL round-bottomed flask immersed on an ice bath at 0 °C were added successively and under stirring MAA (42.8  $\mu$ L, 0.5 mmol) or acrylamide (36 mg, 0.5 mmol), EGDMA (0.48 mL, 2.5 mmol), deltamethrin (63.1 mg, 0.125 mmol), and dichloromethane (2.4 mL). The 1,1'-azobisisobutyronitrile (40 mg, 0.24 mmol) was added afterwards to the reaction mixture. The mixture was sonicated under a nitrogen atmosphere for 10 min in an ice bath, and then stirred in an oil bath at 60 °C. After 24 h,

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