



# A new extraction phase based on a polymer inclusion membrane for the detection of chlorpyrifos, diazinon and cyprodinil in natural water samples



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## ABSTRACT

A simple and effective method for the detection of three pesticides (chlorpyrifos, diazinon and cyprodinil) is developed using a polymer inclusion membrane (PIM) prior to gas chromatography and mass spectrometry detection (GC-MS). Analytes are extracted from natural water samples using a 3 cm<sup>2</sup> PIM made of the polymer, cellulose triacetate (CTA), and the plasticizer, nitrophenyl octyl ether (NPOE). Addition of the plasticizer to the CTA matrix is found to be necessary for the extraction of pesticides. After extraction, analytes are recovered from the membrane with 1 mL of acetonitrile and injected into the GC-MS system. The main factors affecting the extraction efficiency are evaluated, including membrane composition, stirring mode, extraction and elution time. Ultrasonic assisted elution of the extracted pesticides is accomplished after 15 min of contact. The PIM-assisted extraction method makes it possible for pesticides to be determined in the range of 50–1000 ng L<sup>-1</sup> with good linearity (coefficient of determination  $\geq 0.995$ ) and suitable recoveries (85–119%) and precision ( $< 21\%$ ,  $n = 3$ ) using 100 mL of a water sample. This methodology is shown to be suitable for the detection of chlorpyrifos in local river waters.

## 1. Introduction

An ever-increasing world population placing pressure on global food supplies, energy resources and the environment has led to agrochemicals being used not only to protect crops from pests but also to enhance crop yields [1]. Many pesticides used in agriculture are highly toxic both to the environment and to living organisms when their application is uncontrolled. Storm runoff events can cause pesticides to be mobilized from fields to waterbodies. Due to their highly persistent properties, pesticides bioaccumulate in food and can present a risk to animal and human health [2]. Chlorpyrifos (CP), diazinon (DZ) and cyprodinil (CYP) are three of the most widely used pesticides. CP and DZ belong to the organophosphate pesticides chemical family (OPPs). OPPs, like some nerve agents, inhibit a neuromuscular enzyme that is essential for normal function in insects, humans and many other animals. CP is considered by the World Health Organization to be moderately hazardous to humans and more than 10,000 related human deaths a year are reported. CYP is a fungicide which belongs to the family of aminopyrimidines. Aminopyrimidines play an important role in biological processes, since the pyrimidine ring is present in several vitamins, nucleic acids, and coenzymes. The European Water Framework Directive [3] recognizes CP as a priority pollutant and has set

0.1  $\mu\text{g L}^{-1}$  as the maximum concentration permitted in fresh waters. Furthermore, a maximum level for individual pesticides of 0.1  $\mu\text{g L}^{-1}$  has been established in water intended to be used for drinking purposes.

Chromatographic techniques have been extensively used as they are powerful separation techniques and enable the analysis of pesticide residues. However, extraction and concentration is needed prior to chromatographic separation and detection to make the sample more amenable to the analytical techniques and to separate the analytes of interest from other interfering species [4]. Sample preparation is therefore an important step in the analytical process. Conventional methods such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are labour-intensive and environmentally harmful [5,6]. As a result, considerable effort has been devoted to the development of novel sample preparation methods, such as stir bar sorptive extraction [7], solid-phase microextraction (SPME) [8], membrane assisted liquid–liquid extraction [9], single drop microextraction [10], and dispersive liquid–liquid microextraction [11]. Recently, new sample treatment approaches [12–14] and new materials (sorbents) for pesticide extraction have also been explored. In this respect, magnetic molecularly imprinted polymers [15] and magnetic graphene nanoparticles [16] have been described. Moreover, thin films based on polydimethylsiloxane (PDMS) [17], silicone rods and silicone tubes [18],

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and microporous polypropylene hollow-fibre (HF) membranes [9] can be used directly as solid sorbents to extract target species based on an adsorption mechanism.

Extraction of the compounds of interest from water samples can also be achieved with a new class of membranes called polymer inclusion membranes (PIM). These new membranes consist of a base polymer, usually polyvinyl chloride (PVC) or cellulose triacetate (CTA) and a plasticizer. The role of the plasticizer is to increase both the flexibility and the softness. Additionally, plasticizers can modify the solubility properties of the sorbent due to their different polarities and dielectric constants. A third component, an organic extractant or carrier, is needed when separation of species relies on a transport mechanism. Ease of preparation, stability, and mechanical strength are noticeable features of PIMs, which have found many applications in transport systems for the separation and recovery of inorganic species and organic compounds [19,20]. Moreover, membranes made of CTA and the extractant Aliquat 336 have been used as the extraction phase for the preconcentration of trace amounts of several metals such as Cd (II) [21], Cr(VI) [22], Pd(II) and Pt(IV) [23] in complex liquid samples such as electroplating solutions and sea water samples. Once the metals were extracted by the PIM, analysis of the membrane by X-ray fluorescence showed this PIM-assisted extraction to be an easy way to improve the instrumental sensitivity for the detection of these metals. However, the use of PIMs as an extraction phase for organic compounds has yet to be fully exploited.

In this study our intention is to evaluate the use of PIMs as an extraction phase for pesticides prior to their determination using gas chromatography coupled to mass spectrometry. We have studied membranes made of CTA as a polymer and nitrophenyl octyl ether (NPOE), dibutyl sebacate (DBS) and bis (1-butylpentyl) adipate (BBPA) as plasticizers. The extraction efficiency of the different membranes has been evaluated for three pesticides, CP, DZ and CYP. Parameters such as the kinetics of the extraction process as well as elution conditions using different organic solvents such as methanol and acetonitrile (ACN) have also been studied. Moreover, the PIM-assisted extraction for the determination of these pesticides has been validated in a GC-QqQ system. To the best of our knowledge, this work constitutes the first application of a PIM as an extraction phase for the preconcentration of pesticides in river waters.

## 2. Experimental

### 2.1. Chemicals and standards

All reagents and solvents used in this study were of analytical grade. CP, DZ and CYP were obtained from Sigma-Aldrich (Steinheim, Germany). The structure and physico-chemical properties of the studied compounds are shown in Fig. S1 and Table S1. Chlorpyrifos-d10 from Dr. Ehrenstorfer GmbH (Augsburg, Germany) was selected as the internal standard (IS). Other reagents (CTA, NPOE, DBS and BBPA), were obtained from Sigma-Adrich (Steinheim, Germany). Sodium chloride was purchased from Fisher Chemical (Fair Lawn, NJ, USA). Ultrapure water from a Milli-Q Plus water purification system (Millipore Ibérica S.A., Barcelona, Spain) was used. All solvents employed in this study were HPLC-hypergradient. Methanol and trichloromethane were purchased from Panreac (Castellar del Vallès, Spain). ACN was acquired from Fisher Chemical (Fair lawn, NJ, USA).

Stock standard solutions of all pesticides (containing about 500 mg L<sup>-1</sup>) were prepared in methanol. Intermediate solutions of each pesticide (5 mg L<sup>-1</sup>) were also prepared in methanol and replaced every week. All these solutions were stored in darkness at 4 °C.

Water samples were collected from different rivers in Catalonia (north-east Spain): Riells River (pH of 8.15, a conductivity of 99 µS, and total organic carbon (TOC) of 1.81 mg C L<sup>-1</sup>), sampled in the Montseny Natural Park; Ter River (pH of 8.08, a conductivity of 628 µS, and TOC of 27.80 mg C L<sup>-1</sup>), sampled in l'Estartit close to the mouth of the river;

Tordera River (pH of 7.99, a conductivity of 624 µS, and TOC of 5.98 mg C L<sup>-1</sup>), located between the province of Girona and Barcelona; and Llèmena River (pH of 8.24, a conductivity of 318 µS, and TOC of 2.16 mg C L<sup>-1</sup>), in the Garrotxa county. Samples, which were collected during the summer and autumn of 2016, were immediately filtered through a 0.45 µm cellulose acetate membrane filter and stored in darkness at -18 °C in glass bottles.

### 2.2. Equipment and chromatographic conditions

#### 2.2.1. GC-ITMS

Preliminary studies, evaluation of extraction conditions and PIM composition were performed using a Trace GC 2000 coupled to a PolarisQ ion trap mass spectrometer detector (Thermo Scientific, Waltham, MA, USA). A TG-5SIL MS capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) (Thermo Scientific) was used and the carrier gas was 99.9990% pure helium (Carburos Metálicos, Barcelona, Spain) at a constant flow rate of 1 mL min<sup>-1</sup>. The split/splitless injection port was equipped with a 0.75 mm ID liner and operated in splitless mode (maintained for 1 min) at 250 °C (270 °C and 5 min for SPME experiments).

The oven temperature programme started at 80 °C, was held for 2 min; then ramped up to 300 °C at 10 °C min<sup>-1</sup>, and held for 6 min; the total run time was 30 min. Ionization was performed in the electron impact mode at 70 eV. The transfer line temperature was set at 250 °C and the ion source temperature at 225 °C. MS analyses were conducted in full acquisition mode with an *m/z* range from 40 to 400 amu. Peak areas of the compounds were obtained from XIC chromatograms with the following *m/z* ions: 314 and 197 for CP, 225 and 224 for CYP, 304 and 179 for DZ (adapted from Correia et al. [24]). Data analysis was performed using Xcalibur 1.4 software (Thermo Scientific).

#### 2.2.2. GC-QqQ

Method validation and determination of pesticides in river water samples were performed by Trace GC Ultra gas chromatograph equipped with a Triplus™ autosampler coupled to a TSQ Quantum triple quadrupole mass spectrometer system (Thermo Fisher Scientific). Chromatographic separation was performed using a Trace GOLD TG-5SILMS column from Thermo Fisher Scientific (30 m × 0.25 mm i.d. × 0.25 µm). The injector was operated in splitless mode (maintained for 1 min) at 250 °C. The oven temperature program was as follows: initial temperature 60 °C, held for 2 min; then ramped up to 300 °C at 10 °C min<sup>-1</sup>, and held for 6 min; the total run time was 30 min. Mass spectrometric ionization was carried out in electron impact (EI) ionization mode with an EI voltage of 70 eV and a source temperature of 250 °C. Detection was performed in Selected Reaction Monitoring mode (SRM), using the ions indicated in Table S2. The acquired data were processed by TraceFinder EFS 3.1 software.

### 2.3. Preparation of the PIM

Membranes with a composition of 70% polymer and 30% plasticizer (w/w) were prepared according to the procedure found in the literature [25]. In summary, 200 mg of CTA were dissolved in 20 mL trichloromethane and maintained under stirring for 5 h. 90 mg of plasticizer were then added and the resulting mixture was stirred for 2 h more. Different plasticizers (NPOE, DBS and BBPA) with similar viscosity values but different dielectric constants were tested (see Table S3). The mixture was then poured into a 9.0 cm diameter flat bottom glass petri dish, which was set horizontally and covered loosely. The organic solvent was allowed to evaporate over 24 h at room temperature, and the resulting film was then carefully peeled off the bottom of the petri dish. Circular pieces with an area of 3 cm<sup>2</sup> were cut from its central section and used in extraction experiments.

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