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Dual sorbent coating based magnet-integrated fabric phase sorptive extraction as a front-end to gas chromatography–mass spectrometry for multi-class pesticide determination in water samples

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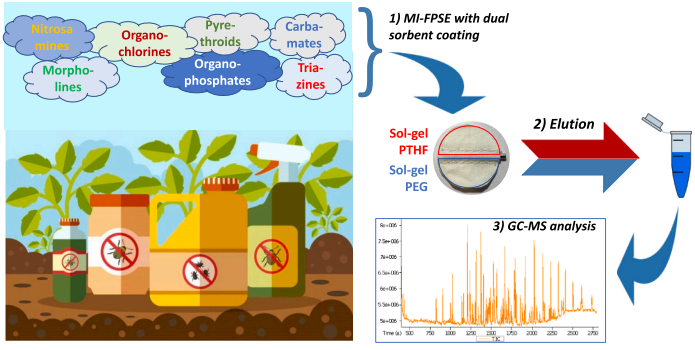
HIGHLIGHTS

- First report of a dual-sorbent magnet-integrated fabric phase sorptive extraction (MI-FPSE) device
- Evaluation of dual sorbent MI-FPSE devices with three different sorbent combinations
- Successful use of dual sorbent MI-FPSE devices for pesticide residue analysis by GC-qMS
- Low solvent waste sample preparation protocol for pesticide determination in water samples

GRAPHICAL ABSTRACT



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ABSTRACT

Magnet-integrated fabric phase sorptive extraction (MI-FPSE) is a sample preparation technique that has proved to be a powerful tool for environmental analysis. The fabrication and application of magnet-integrated dual sorbent-based FPSE membrane prepared by combining two different sol-gel sorbent-coated disks of different polarities together with a magnetic bar inserted between the two membranes to allow the stirring, was examined as novel preparation technique that not required samples pretreatments. The dual sorbent-based sample preparation platforms (made up of poly(tetrahydrofuran) and Carbowax 20M) were used for the extraction of seven classes of pesticides from ambient surface water samples prior to their determination by gas chromatography–mass spectrometry. Initially, different single and dual sol-gel sorbent-based MI-FPSE membranes were evaluated in terms of their extraction efficiency. The MI-FPSE with dual sol-gel sorbents were found to be

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superior to the single-materials MI-FPSE devices in terms of extraction recovery. The main parameters affecting the MI-FPSE extraction protocol (e.g., adsorption time, sample volume, stirring rate, salt addition, eluent type, desorption time and elution volume) were investigated. The selected extraction protocol enabled detection limits in the range between 0.001 and 0.16 ng mL^{-1}. Furthermore, good relative standard deviation values for the intra-day and inter-day repeatability studies were obtained and were lower than 5.9 and 9.9 %, respectively. The proposed method was successfully used for the multi-class analysis of environmental surface water samples.

1. Introduction

Many different classes of synthetic and natural pesticides are widely used in modern agricultural production to maximize harvest yields and simultaneously control insects, fungi, bacteria, weeds, and other pests (Chang et al., 2016). Pesticides are attributed to various health risks including acute gastrointestinal, neurological, and dermatological symptoms, while chronic exposure to them can result in carcinogenic, mutagenic, and toxic effects (Iqbal et al., 2020). Organochlorines, organophosphates, carbamates, pyrethroids and neonicotinoids belong to the most popular classes of pesticides. These compounds exhibit high potential for the contamination of aquatic ecosystems mainly surface and groundwater depending on their water solubility, persistence, and soil mobility (da Silva Sousa et al., 2021). Thus, the development of accurate and sensitive analytical methodologies to assess the levels of these compounds in environmental samples is of high importance.

Both high performance liquid chromatography (HPLC) and gas chromatography (GC) serve as two well-established analytical tools for pesticide residue determination. The coupling of these instrumental techniques with mass spectrometry (MS) can provide analytical methods with excellent precision, accuracy and sensitivity (Iqbal et al., 2020; da Silva Sousa et al., 2021). However, due to the low concentration of the target analytes in environmental sample matrices in combination with the potential co-existence of interfering compounds, an extraction and preconcentration step is typically required (da Silva Sousa et al., 2021; Muckoya et al., 2020).

Multi-class pesticides monitoring sample preparation protocols must be easy to perform, they must result in high selectivity without complicated clean-up strategies, and they must enable the determination of a broad range of analytes (Rejczak and Tuzimski, 2015). At the same time, these protocols should be characterized by minimum organic solvent consumption, high sample throughput and low cost to meet the principles of Green Analytical Chemistry (Armenta et al., 2008) and the recently introduced principles of Green Sample Preparation (López-Lorente et al., 2022). To date, a plethora of novel sample preparation approaches have arisen, aiming to minimize the impact of conventional extraction approaches on the environment. Examples of such methodologies used for multi-class pesticides determination in environmental, food and biological samples include solid-phase microextraction (SPME) (Sakamoto and Tsutsumi, 2004), single drop microextraction (SDME) (Pano-Farias et al., 2017), dispersive solid-phase extraction (dSPE) (Arnnok et al., 2017), stir bar sorptive-dispersive microextraction (Madej et al., 2019), quick, easy, cheap, effective, rugged, and safe (QuEChERS) (Iqbal et al., 2020; Ferracane et al., 2021), magnetic matrix solid-phase dispersion (Binellas and Stalikas, 2015) and fabric phase sorptive extraction (FPSE) (Celeiro et al., 2020; Chen et al., 2021).

FPSE is an evolutionary sample preparation approach that utilizes a natural or synthetic fabric substrate, chemically coated with a sol–gel organic–inorganic hybrid sorbent. The FPSE membranes are characterized by permeability and flexibility, resulting in versatile and user-friendly microextraction devices (Kabir and Samanidou, 2021). Moreover, a wide variety of sorbent materials with good extraction efficiency and rapid extraction equilibrium can be utilized (Kazantzi and Anthemidis, 2017). As a result, FPSE is characterized by tunable selectivity and adjustable porosity, as well as reduced consumption of organic solvents and minimized sample preparation workflow (Manousi et al., 2021). Along with multi-residual protocols, FPSE has been successfully used for the extraction of single classes of pesticides in different environmental and food matrices. Typical examples of FPSE applications in pesticides monitoring include the extraction of organophosphorus pesticides from vegetable samples (Kaur et al., 2019a), the extraction of organochlorine pesticides residues from fruit juices and water samples (Kaur et al., 2019b), the extraction of pirimicarb and fenitrothion from water samples (Ulusoy et al., 2020) and the extraction of triazine herbicides from environmental waters (Roldán-Pijuán et al., 2015) and fruit juices (Manousi et al., 2022a).

Recently, we demonstrated the applicability of magnet-integrated fabric phase sorptive extraction (MI-FPSE) as a stand-alone extraction device for the monitoring of benzoyl urea insecticides in water samples (Manousi et al., 2022b). MI-FPSE utilizes an adaptable extraction device constructed from two FPSE membranes sandwiched together. The extraction devices integrate the stirring mechanism since they also contain a metallic magnetic stirrer placed between the two membranes (Chang et al., 2016). As it is highlighted in the ten principles of Green Sample Preparation, integrating of sample preparation steps can result in enhanced operational simplicity, increased sample throughput, while it is also related with additional benefits (e.g., limited contamination) (López-Lorente et al., 2022). Moreover, the integration of extraction and agitation elements in the same device can efficiently simplify the extraction process, prevent analyte losses due to unintended retention on external devices, and increase the yield of the extraction (Cárdenas and Lucena, 2017). Until now, MI-FPSE has proved to be a useful analytical tool in biological (Alampanos et al., 2021), environmental (Manousi et al., 2022b) and food sample analysis (Manousi et al., 2022c). An important aspect of this technique is the possibility to combine FPSE membranes of different polarities to serve as a useful extraction platform for the simultaneous extraction of a wide range of analytes that exhibit different physicochemical properties. However, this feature has not been explored yet to the best of our knowledge.

In this study, a simple and rapid MI-FPSE protocol was developed, aiming to exploit the features of this technique in multi-class environmental analysis. In order to obtain full advantage of the possibility to synthesize multi-sorbent platforms, MI-FPSE membranes possessing dual sorbent coatings were prepared through the combination of FPSE membranes that exhibit different polarities. The dual sorbent-based microextraction platforms were examined for their performance and MI-FPSE was used as a front-end to gas chromatography–mass spectrometry (GC–MS). The main factors that influence the performance of the MI-FPSE method were studied to ensure high extraction efficiency of the multi-class analytes. Accordingly, the proposed procedure was validated and employed for the monitoring of pesticide levels in environmental waters as a proof-of-concept.

2. Experimental

2.1. Standards, chemicals, and samples

Substrates, chemicals, polymers, catalysts, and solvents used in creating fabric phase sorptive extraction membranes were of the highest quality available in the marketplace. Fabric substrates for FPSE membranes, 100 % cotton cellulose and 100 % polyester fabrics were purchased from JoAnn Fabric (Miami, FL, USA). Polymers, Carbowax 20M (CW 20M) and poly(tetrahydrofuran) (PTHF), sodium hydroxide, hydrochloric acid, and methyl trimethoxysilane were purchased from

Sigma-Aldrich (St. Louis, MO, USA). Poly(caprolactone)-*block*-poly (dimethylsiloxane)-*block*-poly(caprolactone) (PCAP-PDMS-PCAP) block copolymer was purchased from Gelest Inc. (Morrisville, PA, USA). Solvents, dichloromethane and acetone were purchased from Fisher Scientific (Milwaukee, WI, USA).

To obtain homogeneous sol solutions, an Eppendorf Microcentrifuge Model 5415R (Eppendorf North America Inc., Hauppauge, NY, USA) was used. A Fisher Scientific Digital Vortex Mixture (Fisher Scientific, Pittsburg, PA, USA) was used to ensure thorough mixing of different solutions. The sol solution was sonicated in a 2510 BRANSON Ultrasonic Cleaner (Branson Ultrasonics, Danbury, USA) to obtain bubble-free sol solution. A Barnstead Nanopure Diamond (Model D11911) deionized water unit (Dubuque, IA, USA) provided ultra-pure deionized water (18.2 MΩ cm^{-1}) for sol-gel synthesis and substrate treatment in the lab where the FPSE membranes were produced.

Forty-one pesticides reference standards (purity ≥98 %) of different classes (carbamates, morpholines, nitrosamines, organochlorines, organophosphates, pyrethroids, and triazines) were employed in this work and purchased from Supelco (Bellefonte, PA, USA) and Dr. Ehrenstorfer Gmbh (Augsburg, Germany).

A stock solution containing all the compounds at a concentration of 20 μg mL^{-1} was prepared in acetone. The stock solution was diluted at different concentration levels to construct the calibration curve with pure standard solutions and the matrix-matched calibration. All the solutions were stored in amber glass vial at 4 °C until their use.

Methanol (MeOH) and acetonitrile (ACN) of LC-MS grade were purchased from Honeywell (Charlotte, North Carolina, USA). HPLC grade acetone was purchased from Merck Life Science (Darmstadt, Germany). Sodium chloride was purchased from Merck Life Science. Ultrapure water was produced by using a Milli-Q system Plus purification system (Millipore, Bedford, MA, USA).

Three environmental water samples, namely river water, pond water, and lake water, were collected in the municipal area of Vienna and stored in amber glass bottle without headspace at 4 °C until use. The samples were not subjected to any pretreatment before analysis.

2.2. Instrumentation

The analyses were performed on a GC-2010 gas chromatograph system equipped with a split/splitless injector, an AOC-5000 multifunctional autosampler, and a QP2010 Ultra mass spectrometer (Shimadzu Corporation, Kyoto, Japan). Data collection and processing was conducted using GCMS Solution v.4.50 software (Shimadzu), while MS spectral matching was performed by using the Pesticides II Edition MS spectral library (Shimadzu Europe, Duisburg, Germany). The separation of the target analytes was carried out on a Rtx-5MS (30 m × 0.25 mm ID, 0.25 μm d_f) column (Restek Corporation, Bellefonte, PA, USA) at constant linear velocity (35 cm s^{-1}) by using helium as carrier gas. The initial column oven temperature was 40 °C and it was raised up to 330 °C at a rate of 10 °C min^{-1}. Sample injection was performed under high-pressure conditions (500 kPa for 0.5 min). The injection volume was 3 μL and it was conducted at splitless mode for (1 min), while a gas saver split ratio of 1:5 was set at 2 min. The injector temperature was 280 °C.

Electron ionization mode was chosen for analyte ionization (70 eV), while interface and ion source temperatures were set at 250 °C and 200 °C, respectively. The identification of the target analytes was conducted at an acquisition scan mode at a mass range of *m/z* 40–500. The selected ion monitoring (SIM) parameters and the retention times of the target analytes are summarized in Table S1 (Electronic Supplementary Information).

2.3. Preparation of fabric phase sorptive extraction membranes and the fabrication of MI-FPSE devices

Due to the broad range of physicochemical properties of the target pesticides investigated in the current study from complex environmental sample matrices, it is unlikely that a single sol-gel sorbent-coated FPSE membrane would be able to extract and preconcentrate all the analytes with uniform extraction efficiency. As such, three different sorbent coated fabrics, widely varied in their overall polarity, were synthesized, and evaluated that include: sol-gel CW 20 M, sol-gel PCAP-PDMS-PCAP and sol-gel PTHF. Sol-gel sorbent coatings were created on cotton fabric (100 % cellulose) as well as on 100 % polyester fabric. Sol solutions for creating the surface coating on the fabric substrates were prepared by the sequential addition of the polymer, sol-gel precursor methyl trimethoxysilane (MTMS), mixed solvent system methylene chloride: acetone (50:50 *v*/v) sol-gel catalyst trifluoroacetic acid (TFA) and water as the hydrolytic agent into a glass reaction vessel. Relative molar ratio between the polymer: sol-gel precursor: acetone: methylene chloride: catalyst: water was maintained at 1: 7.1 × 10–3: 1.94: 2.3: 0.75: 3 for sol-gel CW20 M; 1: 0.57: 1.94: 2.3: 0.75: 3 for sol-gel PTHF; and 1: 0.025: 1.94: 2.3: 0.75: 3 for sol-gel PCAP-DMS-PCAP. The pretreatment of the cellulose fabric substrate prior to the sol-gel coating, the sol-gel dip coating process to create chemically bonded sorbent coatings on the substrate surface, and conditioning and cleaning of the sol-gel sorbent coated FPSE membranes have been described extensively elsewhere (Alampanos et al., 2021; Płotka-Wasylka and Wojnowski, 2021). Sol-gel sorbent-coated FPSE membranes were prepared as large planar sheets (45 cm × 15 cm). For the single sorbent-based MI-FPSE device, two planar sheets of sol-gel sorbent-coated membranes were stitched together with a 3 cm pocket at the center of the disks. Subsequently, the sandwiched disks were carefully cut at 1.50 cm diameter (radius 0.75 cm). A magnet (1/2″ × 1/16″) was then inserted into the pocket between the two sol-gel sorbents coated FPSE disks that results in a magnet-integrated FPSE device (MI-FPSE device). For dual sorbent-based MI-FPSE device, two planar sheets of different sol-gel-sorbent coated FPSE membranes were used.

2.4. MI-FPSE procedure

The dual sol-gel sorbent-based MI-FPSE membranes were prepared in the laboratory by combining the two phases which showed the best results in terms of extraction efficiency. Prior to their use, the MI-FPSE membranes were immersed in 2 mL of an ACN: MeOH (50:50, *v*/v) solution to remove residues from manufacturing and to activate the membranes. Subsequently, the MI-FPSE membranes were washed thoroughly with deionized water in order to remove any traces of organic solvent that could interfere with the extraction of the pesticides. For pesticide uptake, 100 mL of milli-Q water was transferred to a 150 mL glass bottle and the ionic strength was adjusted by adding 5 % *w/v* NaCl. The sample was placed on a magnetic stirrer (Heidolph Instruments GmbH & Co, Schwabach, Germany) and the extraction was carried out at 1000 rpm for 50 min. After extraction, the MI-FPSE membranes were rinsed with deionized water in order to remove the presence of salt from the membranes. Subsequently, after drying with lint-free tissue, the membranes were placed in an Eppendorf safe-lock tube and the elution of the analytes was carried out by adding 250 μL of acetone and vortexing for 2 min. At the end the solvent was filtered using 0.22 μm polytetrafluoroethylene filters (Frisenette ApS, Knebel, Denmark) and the eluent was analysed for the determination of the target analytes. After a complete extraction/elution cycle, the MI-FPSE membranes were washed with 2 mL of ACN: MeOH (50:50, *v*/v) solvent mixture to remove any residue of sample matrix or analyte from the previous use.

3. Results and discussions

3.1. Characterization of the FPSE devices

FPSE membranes coated with sol-gel PTHF and sol-gel CW 20M were characterized using Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy, to investigate the functional make

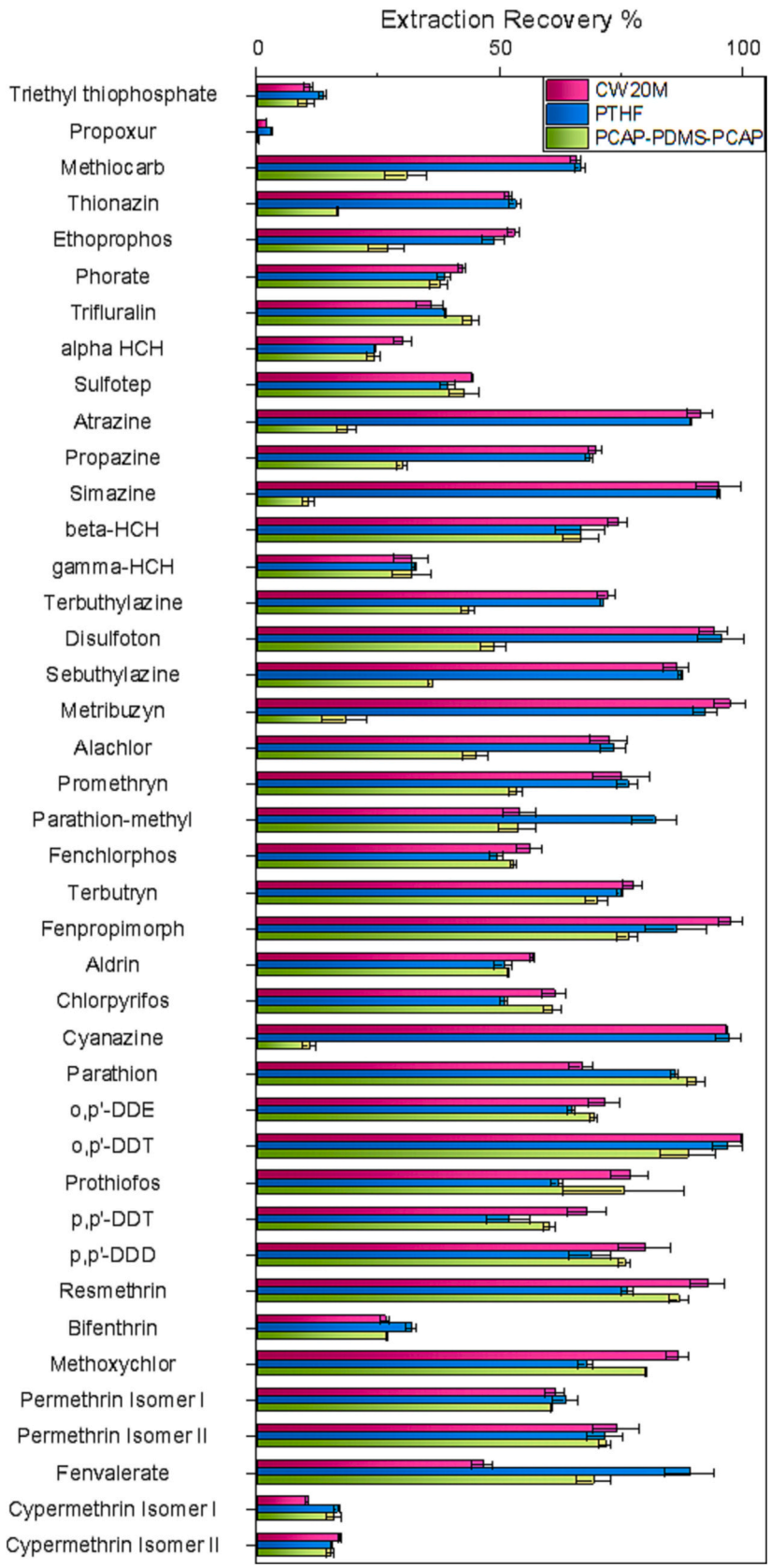

Fig. 1. Evaluation of different sol-gel materials. Concentration of target analytes: 1.0 ng mL^{-1}, NaCl content: 0 % *w/v*, sample volume: 20 mL, adsorption time: 30 min, stirring rate: 1000 rpm, eluent: methanol, eluent amount: 0.5 mL, elution time: 5 min.

up the sol-gel sorbents and the surface morphology of the sol-gel sorbent coated FPSE membranes, respectively. These results are reported elsewhere (Manousi et al., 2022c; Roldán-Pijuán et al., 2015).

3.2. Development of the sample preparation protocol

The extraction protocol was optimized in order to obtain the best compromise for all the compounds of the different classes examined. The first step involved testing three different sol-gel sorbent materials, namely sol-gel PTHF (medium polarity sorbent), sol-gel CW 20M (polar sorbent) and sol-gel PCAP-PDMS-PCAP (polar-nonpolar composite sorbent) coated on two different fabric substrates (i.e., cellulose and polyester). Following the selection of the most appropriate sol-gel sorbents and substrates, three different dual sorbent-based MI-FPSE platforms were created by combining two different sol-gel sorbent materials at a time, given the widely different physicochemical characteristics of the compounds under examination. Taking into consideration, the different substrates, and sol-gel materials available, dozens of combinations involving the use of two or more sorbent materials at a time may be fabricated.

The second step involved testing the effect of the main factors (sample volume, adsorption, and desorption time, stirring rate, desorption solvent and relative volume, and salt content) on the extraction efficiency of the MI-FPSE process. The investigation of the adsorption and elution steps was performed using the one-variable-at a time (OVAT) approach. Table S2 (Electronic Supplementary Information) summarized the initial, investigated, and selected parameters. All experiments during method development were performed in duplicate and their standard deviations are presented in the respective figures.

3.2.1. Evaluation of different MI-FPSE devices

The first step of this work was based on the investigation of the adsorbent phase to be used for the extraction of target compound of different chemical class. Three MI-FPSE polyester platforms consisting of two sandwiched membranes of the same sol-gel coatings (i.e., sol-gel PTHF, sol-gel CW 20M and sol-gel PCAP-PDMS-PCAP) were initially investigated. The graph in Fig. 1 shows that the two adsorbent materials CW 20M and PTHF showed good extraction efficiency for all the analytes investigated in this work. Sol-gel CW 20M MI-FPSE membranes resulted in better extraction efficiencies for ethoprophos, phorate, alpha-HCH, sulfotep, atrazine, propazine, beta-HCH, terbuthylazine, metribuzin, fenchlorphos, terbutryn, fenpropimorph, aldrin, chlorpyrifos, o,p′-DDE, o,p′DDT, prothiofos, p,p′-DDT, p,p′DDD, resmethrin, methoxychlor, permethrin isomer II, and cypermethrin isomer II, while sol-gel PTHF MI-FPSE membranes resulted in better extraction efficiencies for triethyl thiophosphate, propoxur, methiocarb, thiozanin, gamma-HCH, disulfoton, sebuthylazine, alachlor, promethryn, parathion-methyl, cyanazine, bifenthrin, permethrin isomer I, fenvalerate and cypermethrin isomer I. Similar extraction efficiencies were observed for the remaining pesticides. Only in the case of trifluralin and parathion, sol-gel coated PCAP-PDMS-PCAP membranes showed better extraction efficiency. It is noteworthy that the same sol-gel sorbents materials were also evaluated as coatings on cellulose supports. However, reduced extraction efficiency was observed compared to the initially employed polyester coated membranes and thus polyester was chosen as the fabric substrate. The reduced extraction efficiency when the cellulose-based membrane was used, is strictly connected with the physico-chemical extraction characteristics of the here-in proposed technique. It should be underlined that MI-FPSE is an extraction technique that exploits the surface chemistry of the substrate. In fact, the selectivity and extraction efficiency of the membrane derive from the entire combination and in some case synergy of the polymer and the surface chemistry of the substrate (Kabir and Samanidou, 2021).

Following the evaluation of the MI-FPSE membranes consisting of two membranes with the same sol-gel coating, three different dual sorbent-based MI-FPSE membranes were fabricated by combining the

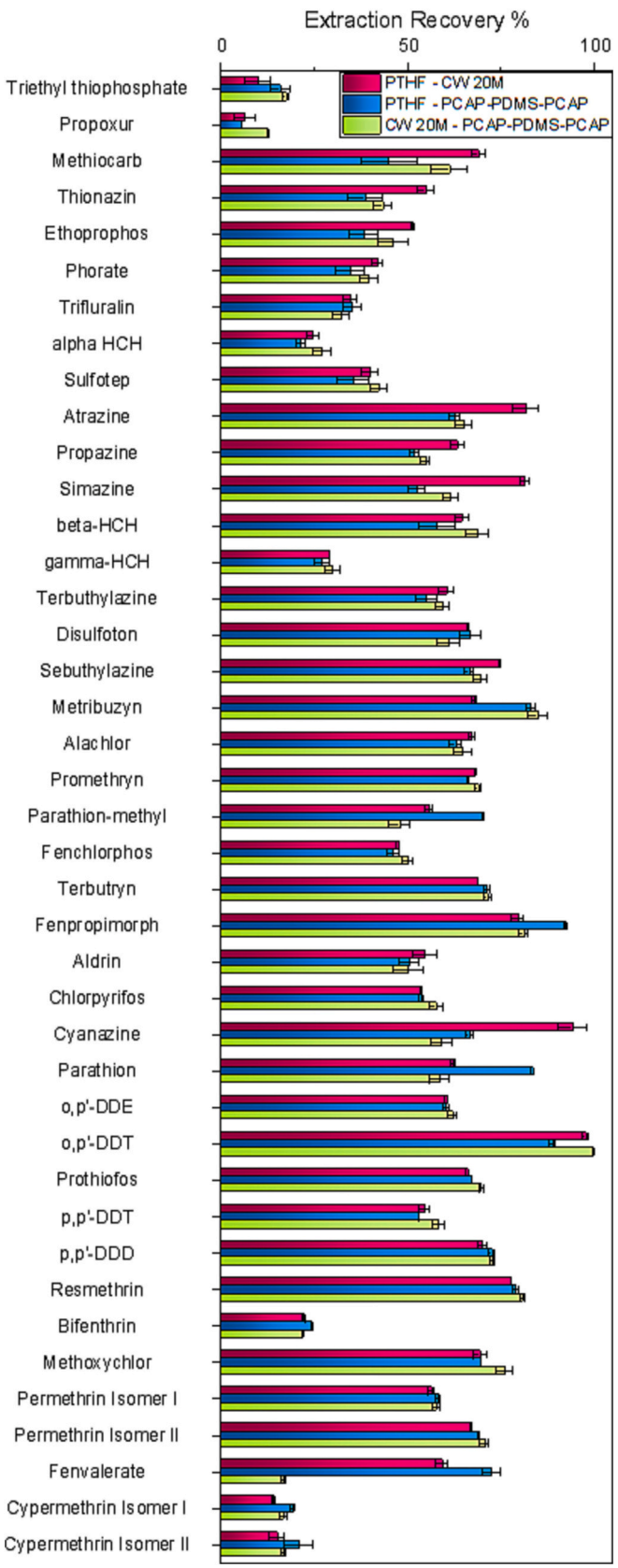

Fig. 2. Evaluation of different dual sol-gel combinations. Concentration of target analytes: 1.0 ng mL^{-1}, NaCl content: 0 % w/v, sample volume: 20 mL, adsorption time: 30 min, stirring rate: 1000 rpm, eluent: methanol, eluent amount: 0.5 mL, elution time: 5 min.

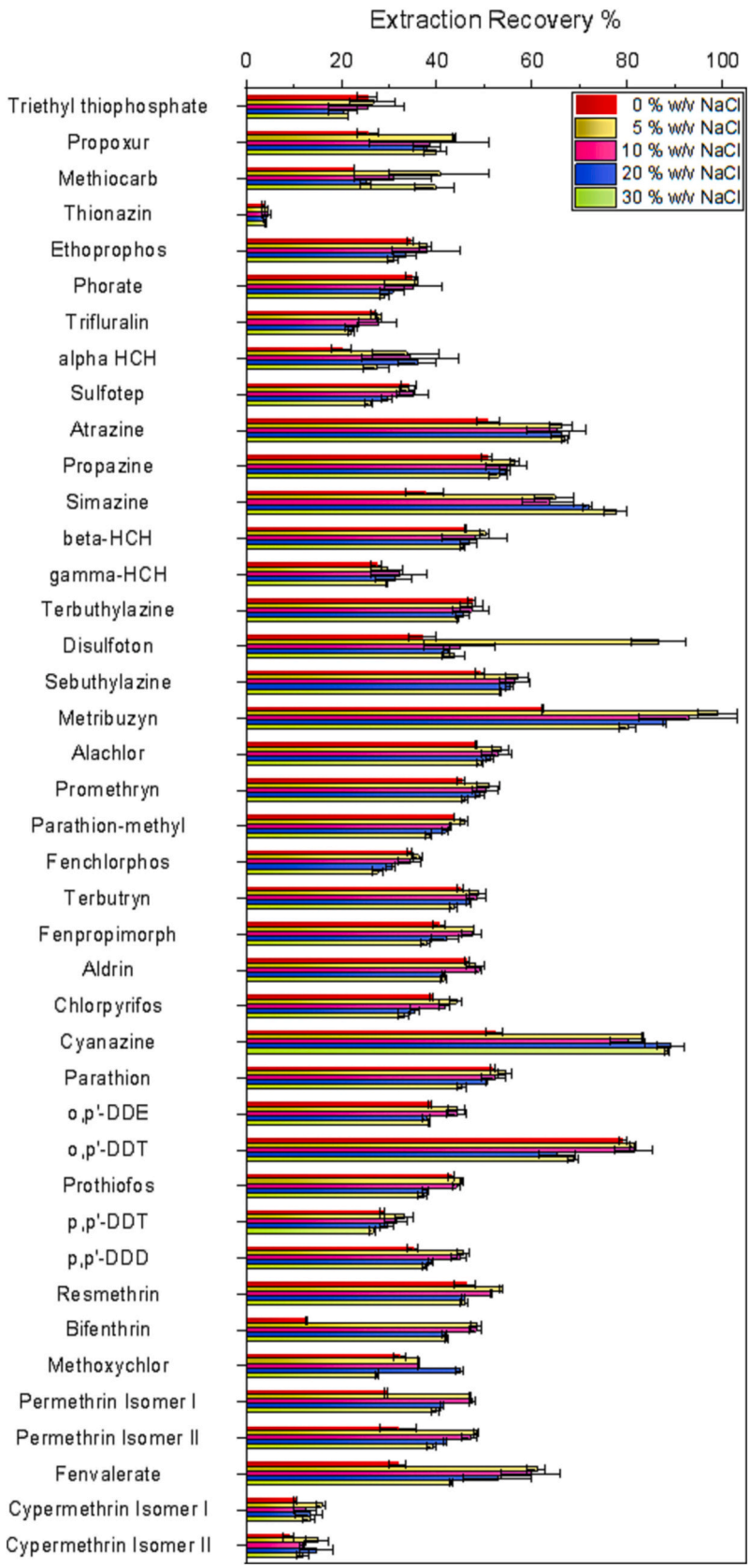

Fig. 3. Evaluation of salt content at different percentage. Sol-gel sorbent: CW 20M – PTHF. Concentration of target analytes: 1.0 ng mL^{-1}, sample volume: 20 mL, adsorption time: 30 min, stirring rate: 1000 rpm, eluent: methanol, eluent amount: 0.5 mL, elution time: 5 min.

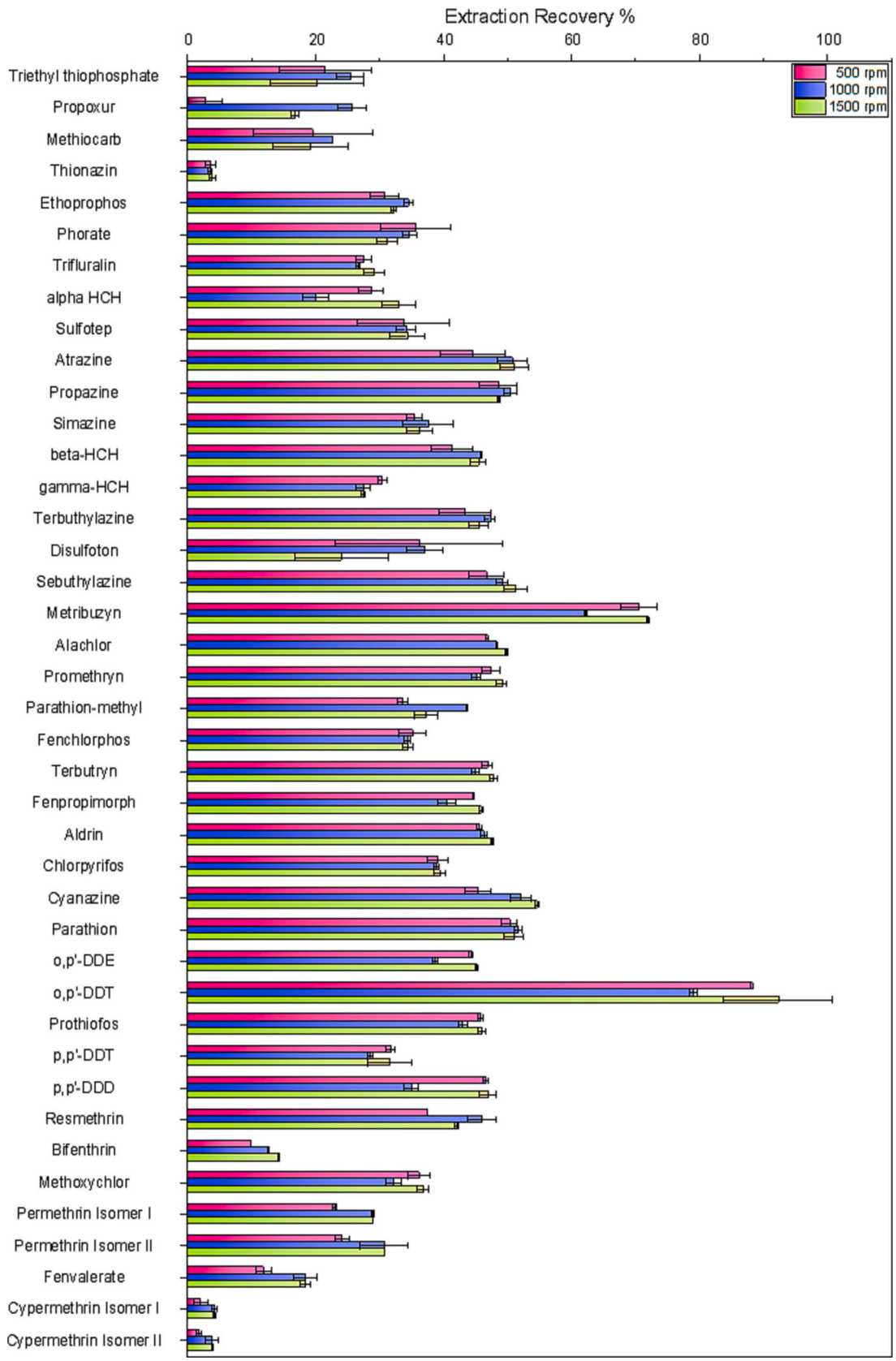

Fig. 4. Evaluation of different stirring rates. Sol-gel sorbent: CW 20M – PTHF. Concentration of target analytes: 1.0 ng mL^{-1}, sample volume: 20 mL, NaCl content: 0 % w/v, adsorption time: 30 min, eluent: methanol, eluent amount: 0.5 mL, elution time: 5 min.

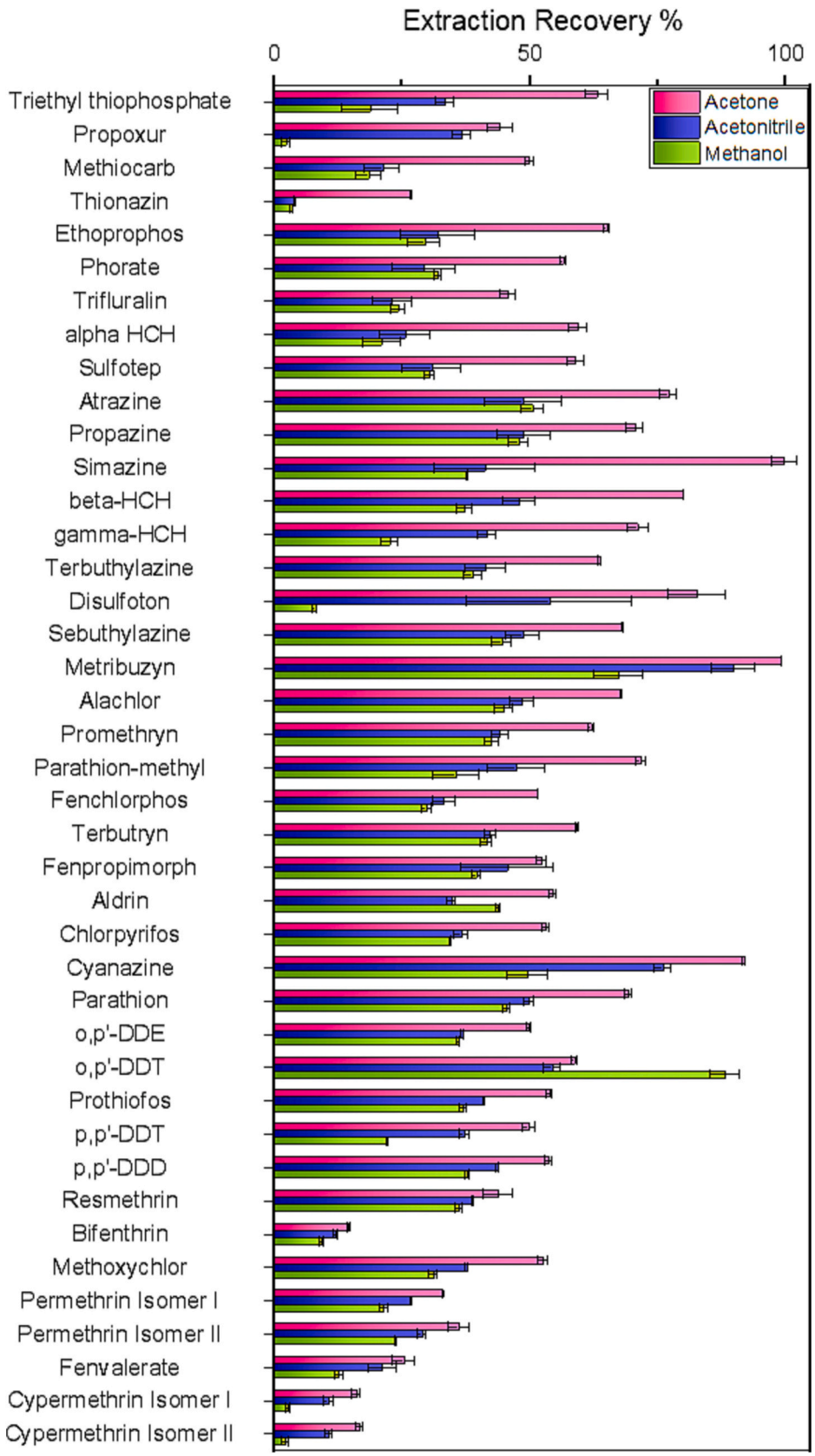

Fig. 5. Evaluation of different eluents. Sol-gel sorbent: CW 20M – PTHF. Concentration of target analytes: 1.0 ng mL^{-1}, sample volume: 20 mL, NaCl content: 0 % w/v, adsorption time: 30 min, stirring rate: 1000 rpm, eluent amount: 0.5 mL, elution time: 5 min.

Table 1
Validation results for the MI-FPSE-GC–MS protocol.

Analyte	Regression analysis	R^2	Linear range (ng mL^{-1})	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	ER%	EF
Triethyl thiophosphate	y = 27,114.6x + 2741.2	0.9978	0.05–5.00	0.02	0.05	99.7	398.7
Propoxur	y = 46,425.9x − 1037.0	0.9988	0.5–10.0	0.16	0.50	19.5	78.0
Methiocarb	y = 95,088.1x − 30,861.6	0.9926	0.2–10.0	0.06	0.20	76.4	305.7
Thionazin	y = 40,539.1x − 3823.8	0.9969	0.05–10.0	0.02	0.05	84.5	337.8
Ethoprophos	y = 51,632.5x − 303.5	0.9990	0.02–5.00	0.006	0.02	93.5	374.1
Phorate	y = 235,399.4x + 4731.3	0.9990	0.01–5.00	0.003	0.01	99.9	399.7
Trifluralin	y = 38,392.7x − 789.0	0.9978	0.01–5.00	0.003	0.01	94.1	376.4
alpha HCH	y = 20,284.6x + 2685.7	0.9980	0.05–5.00	0.02	0.05	97.5	390.1
Sulfotep	y = 86,019.3x + 6948.9	0.9940	0.05–5.00	0.02	0.05	97.3	389.2
Atrazine	y = 48,954.4x + 8595.2	0.9993	0.1–10.0	0.03	0.10	57.5	229.8
Propazine	y = 110,278.8x + 5402.9	0.9981	0.05–10.0	0.02	0.05	84.3	337.2
Simazine	y = 22,702.4x − 5465.3	0.9987	0.1–10.0	0.03	0.10	48.9	195.7
beta-HCH	y = 39,757.8x + 411.1	0.9997	0.1–10.0	0.03	0.10	61.4	245.4
gamma-HCH	y = 9505.1x − 3012.6	0.9933	0.2–5.00	0.06	0.20	84.9	339.5
Terbuthylazine	y = 93,874.9x + 813.0	0.9994	0.01–5.00	0.003	0.01	87.6	350.3
Disulfoton	y = 593,044.8x − 10,483.6	0.9962	0.02–10.0	0.006	0.02	98.1	392.2
Sebuthylazine	y = 131,600.5x + 1928.4	0.9992	0.01–5.00	0.003	0.01	66.2	264.8
Metribuzin	y = 27,350.8x − 2228.2	0.9991	0.05–10.0	0.02	0.05	26.9	107.7
Alachlor	y = 66,558.5x + 4520.4	0.9967	0.05–5.00	0.02	0.05	67.6	270.6
Promethryn	y = 130,677.7x + 5751.8	0.9976	0.01–5.00	0.003	0.01	69.7	278.6
Parathion-methyl	y = 91,391.8x − 15,689.9	0.9971	0.2–10.0	0.06	0.20	78.5	314.1
Fenchlorphos	y = 73,832.4x − 1398.4	0.9992	0.01–5.00	0.003	0.01	91.8	367.3
Terbutryn	y = 99,329.6x + 3098.2	0.9992	0.01–5.00	0.003	0.01	75.9	303.8
Fenpropimorph	y = 686,457.4x + 5270.2	0.9991	0.01–5.00	0.003	0.01	98.7	394.7
Aldrin	y = 70,133.5x + 1739.9	0.9992	0.01–5.00	0.003	0.01	74.3	297.2
Chlorpyrifos	y = 84,113.0x − 1134.5	0.9985	0.02–5.00	0.006	0.02	91.0	364.1
Cyanazine	y = 20,273.6x − 3182.6	0.9977	0.5–10.00	0.16	0.50	50.7	202.7
Parathion	y = 91,090.0x − 5367.2	0.9984	0.02–5.00	0.006	0.02	71.6	286.4
o,p'-DDE	y = 123,774.0x + 6318.1	0.9979	0.01–5.00	0.003	0.01	74.4	297.5
o,p'-DDT	y = 19,022.1x − 1116.9	0.9968	0.004–2.10	0.001	0.004	51.1	204.5
Prothiofos	y = 73,302.9x − 4413.3	0.9969	0.2–10.00	0.06	0.20	80.0	320.1
p,p'-DDT	y = 179,349.1x + 1882.7	0.9991	0.008–4.00	0.003	0.008	89.5	358.0
p,p'-DDD	y = 35,867.2x − 405.9	0.9997	0.02–5.00	0.006	0.02	82.3	329.1
Resmethrin	y = 147,605.3x + 2074.9	0.9983	0.01–5.00	0.003	0.01	69.0	275.9
Bifenthrin	y = 480,459.0x + 31,988.6	0.9988	0.01–5.00	0.003	0.01	67.0	268.0
Methoxychlor	y = 207,692.4x − 5692.7	0.9949	0.01–5.00	0.003	0.01	97.1	388.2
Permethrin isomer I	y = 113,176.7x + 1750.7	0.9992	0.01–5.00	0.003	0.01	76.9	307.5
Permethrin isomer II	y = 159,596.3x + 3595.7	0.9989	0.01–5.00	0.003	0.01	79.3	317.3
Fenvalerate	y = 37,852.3x + 760.9	0.9978	0.01–5.00	0.003	0.01	62.7	250.7
Cypermethrin isomer I	y = 23,790.0x − 1333.1	0.9981	0.1–5.00	0.03	0.10	35.0	139.9
Cypermethrin isomer II	y = 20,676.6x − 4034.3	0.9908	0.1–5.00	0.03	0.10	49.2	196.9

examined extraction phases aiming to take advantage of the difference in their polarities that is directly associated with their performance. As such, the following dual platforms were tested: sol-gel PTHF – CW 20M, sol-gel PTHF–PCAP-PDMS-PCAP, and sol-gel CW 20M– PCAP-PDMS-PCAP. The results of this study are presented in Fig. 2. As it can be observed, the dual sol-gel PTHF – CW 20M platforms exhibited the highest extraction efficiency towards the examined analytes. This observation agrees with the results of the previous investigation in which sol-gel PTHF and sol-gel CW 20M were found to be suitable for different analytes. In fact, the dual MI-FPSE membranes showed better extraction recovery than the single-phase membranes since they enabled to achieve a compromise between the extraction recoveries obtained by the individual sol-gel PTHF and sol-gel CW 20M. Taking into consideration all the forty-one pesticides examined in this work the dual sol-gel PTHF–CW 20M MI-FPSE platforms were utilized for further experiments.

3.2.2. Study of sample volume

One of the most significant factors affecting both the extraction efficiency and the method sensitivity is the volume of the sample solution. In this work, the effect of the sample volume on the extraction efficiency was investigated in a range from 10 mL to 500 mL. The results showed that an increase of the sample volume up to 200 mL, resulted in almost constant extraction recovery values (Fig. S1). A subsequent increase in volume, equal to 500 mL, resulted in a decrease in the extraction efficiency. This trend can be attributed to a non-optimal ratio between the sample volume- and the sorbent phase surface. Taking into consideration the extraction recovery and the enhancement factors for the target analytes, as well as other factors including sample availability, sample transport cost to the laboratories and the principles of GAC (López-Lorente et al., 2022) regarding the minimization of sample consumption, the best compromise was found to be 100 mL of aqueous sample or standard solution. However, in cases that a further increase of the extraction sensitivity may be required, the experimental results show that it is possible to use a sample volume of 200 mL.

3.2.3. Study of salt content

The next parameter that was evaluated in this work was the salt content of the solution. Salt is normally added to aqueous solutions to decrease the solubility of the analytes (by increasing the ionic strength of the solution) and thereby increase the extraction efficiency of the method. For this purpose, in this work the amount of salt was evaluated in the range of NaCl concentrations between 0 and 30 % *w/v*. As evidenced by the results shown in Fig. 3, for most of the pesticides examined in this study the best adsorption conditions were observed when a concentration of 5 % *w/v* NaCl was employed. Only a few exceptions were observed including methoxychlor and cyanazine, alpha-HCH, gamma-HCH, and simazine which showed the best conditions of adsorption at higher NaCl contents. For this reason, a concentration of 5 % w/v of NaCl was selected for the subsequent experiments. Although it has not been the subject of this research, taking into consideration that sea water has a salinity between 2.5 and 3.5 %, the proposed method can

be considered compatible for the analysis of saline waters. Further research exploiting this feature will be conducted in the future.

3.2.4. Study of stirring rate

Sample agitation is one of the parameters that can affect the degree of adsorption of the analytes. In this study, the investigated range of stirring rates was between 0 rpm and 1500 rpm. An increase in the stirring rate from 500 to 1000 rpm resulted in a progressive increase of the adsorption efficiency (Fig. 4). At higher stirring rates for some pesticides investigated in this study, a decrease in the adsorption efficiency was observed and thus further experiments were carried out at 1000 rpm.

3.2.5. Study of adsorption time

The adsorption time of the MI-FPSE procedure was investigated between 5 and 60 min. The results obtained in this study (Fig. S2) showed that short adsorption times (between 10 and 30 min) were not sufficient to obtain extraction equilibrium for the target analytes. An increase of the extraction time up to 40 min resulted in extraction equilibrium for cyanazine, metribuzin and thionazin, However, an adsorption time of 50 min was required for most analytes to reach equilibrium. A further increase up to 60 min, did not result in an increase in adsorption efficiency. Therefore, the adsorption time used in the method was of 50 min.

3.2.6. Study of desorption conditions

Following the evaluation of the adsorption conditions, the main parameters affecting the desorption step (i.e., eluent type, elution mode, eluent volume and desorption time) were evaluated. The study was carried out under the following experimental conditions: MI-FPSE sorbent material: PTHF-CW 20 M, sample volume: 20 mL, extraction time: 30 min, stirring speed: 1000 rpm, salt content: 0 % *w/v* NaCl, eluent volume: 0.5 mL, desorption time: 5 min. Three different eluents were evaluated for desorption of the analytes, namely acetone, acetonitrile, and methanol. As reported in Fig. 5, remarkably better results were obtained using acetone for the desorption of the analytes from the MI-FPSE membranes. It should be noted that only in the case of *o,p′*-DDT a better extraction was obtained when methanol was used as a solvent. Thus, acetone was adopted for further experiments.

The desorption mode and desorption time were then examined. As regards to the desorption mode, the tests were carried out under stirring and in the absence of stirring. Similar extraction efficiencies were observed for all analytes, indicating that the elution of the adsorbed analytes can be performed in the absence of stirring. Another factor studied was the desorption time of the analytes from the membranes to the extraction solvent. In this study desorption time spans between 2 and 15 min were investigated. The recovery values showed that analytes' desorption can be achieved in 2 min, while the prolongation of this time had no significant impact on the extraction efficiency. Thus, elution was performed within 2 min without stirring.

The last parameter studied related to the desorption step was the volume of the solvent used. Three different elution volumes were evaluated, i.e., 250 μL, 500 μL, 1000 μL of acetone. The ratio between the volume of the sample and the desorption solvent are directly correlated with the enrichment factor of the method and for this reason the use of a smaller quantity of desorption solvent allows to have a greater method sensitivity. Furthermore, the use of smaller quantities of organic solvents allows to obtain more eco-friendly methods and is in accordance with the guidelines of GAC (López-Lorente et al., 2022). The experimental data show that the use of 250 μL of solvent is sufficient to elute the adsorbed analytes from the MI-FPSE membranes obtaining the greatest possible enrichment. A lower volume use of desorption solvent would be impractical to use since the complete immersion of the MI-FPSE medium in the eluent cannot be ensured.

3.3. Validation of the MI-FPSE-GC–MS method

The developed MI-FPSE-GC–MS method was validated in terms of linearity, limits of detection (LoDs) and limits of quantification (LoQs), accuracy, and precision. The external matrix-matched calibration curves were constructed, at different levels for the various target compounds (Table 1), by spiking different amounts of standard solution in deionized water. Least squares regression analysis was used to calculate the intercepts, slopes, and coefficients of determination for all target compounds. As shown in Table 1, good method linearity was observed within the examined range since the coefficients of determination were between 0.9908 and 0.9997. The LoQ values were the lowest points on the calibration curves used for each analyte that corresponded to a signal to noise ration higher than 10, while the LoDs values were calculated by dividing the LoQs of each pesticide by 3.3. The LoDs and LoQs of the target analytes were shown in Table 1 and ranged between 0.001 and 0.16 ng $mL^{-1}$and 0.004–0.5 ng mL^{-1} respectively.

The theoretical preconcentration factor (PF) of the developed technique was 400 and was calculated by dividing the initial sample volume (100 mL) by the final volume of solvent used for desorption (250 μL). The enhancement factor (EF) values were then calculated by dividing the slopes of the matrix-matched calibration curves obtained with the MI-FPSE protocol against the slopes of the calibration curves obtained by analysing standard solutions. The EF values ranged from 78.0 to 399.7 for propoxur and phorate, respectively. Moreover, the percentage extraction recovery values (ER%) of the target analytes were calculated by comparing the EF values and the theoretical values of PF multiplied by 100. These values were in the range between 19.5 and 99.9 %.

The accuracy and precision of the MI-FPSE-GC–MS method were subsequently evaluated at two levels of concentration, and they were expressed in terms of relative recovery percentage (RR%) and relative standard deviation (RSDs), respectively. Five repetitions of extraction and analysis were performed on the same day for intra-day study ($n = 5$), while inter-day studies were conducted by performing triplicate analyses of the spiked samples for four consecutive days ($n = 3 \times 4$). The RR % values were calculated by comparing the mean of the experimental concentration with the theoretical concentrations. The areas obtained from the spiked samples analyses were used for the calculation of the standard concentrations through the use of the matrix-matched calibration curves. As shown in Table S3, the RR% values were between 84.1 % and 116.4 % for the intra-day study and between 82.7 % and 116.5 % for inter-day study. Moreover, the precision values of the developed protocol were in the range of 0.6–5.9 % and 2.6–9.9 % for the intra-day and inter-day studies, respectively. The obtained RSD and RR % values indicate a good repeatability and accuracy of the developed protocol. Intra-day and inter-day data were shown in Table S3.

The extraction and analysis method proved to be valid and robust despite not using an internal standard for monitoring extractions and normalization of the target compound areas. In this way, the number of chemical reagents was reduced, keeping the method as green as possible.

3.4. Reusability and potential carry-over of the MI-FPSE devices

The reusability of the dual sorbent-based MI-FPSE membranes and the potential carry-over were also evaluated in this study. To this end, a single MI-FPSE device was used for multiple extraction cycles from spiked lake water samples and the device consider reusable as long as the extraction performance was not reduced by >10 %. Following the first extraction cycle, the MI-FPSE membranes were subjected to a second elution cycle to examine the occurrence of undesirable carry-over effects. In this case, no carry-over was observed not for any of the analytes. Moreover, it was observed that a dual sorbent-based MI-FPSE device can be used for at least 25 consecutive adsorption/desorption cycles without showing significant performance losses. Thus, the herein used extraction phases meets the requirements of Green Sample

Table 2
Comparison of the proposed method with other methodologies.

Sample preparation[a]	Number of analytes	Instrumental technique[b]	Sample amount (mL)	RSD%	Relative recovery %	Theoretical enhancement factor	LOD (ng mL^{-1})	Ref.
DLLME	32	GC–MS/MS	35	3.0–9.0 (inter-day)	90–104 (inter-day)	466	0.3–5.2	(Rubirola et al., 2019)
MSPE	15	GC–MS	4	8.0–16.0 (intra-day) 12.0–18.0 (inter-day)	79.9–111.6	26	0.51–2.29	(Barbosa et al., 2017)
DI-SPME	16	GC–MS	3	1.9–9.6	84.0–119.0	–	0.015–0.13	(Tankiewicz et al., 2013)
SPE	8	LC-MS/MS	100	≤14	65–126	100	0.03–5.10	(Gil García et al., 2017)
MI-FPSE	41	GC–MS	100	0.6–5.9 (intra-day) 2.6–9.9 (inter-day)	84.1–116.4 (intra-day) 82.7–116.5 (inter-day)	400	0.001–0.16	This study

[a] DLLME: dispersive liquid-liquid microextraction, MSPE: magnetic solid-phase extraction, DI-SPME: direct immersion-solid phase microextraction, SPE: solid-phase extraction, MI-FPSE: magnet-integrated fabric phase sorptive extraction.
[b] GC–MS/MS: gas chromatography-tandem mass spectrometry, GC–MS: gas chromatography-mass spectrometry, LC-MS/MS: liquid chromatography-tandem mass spectrometry.

Preparation in terms of materials reusability (López-Lorente et al., 2022).

3.5. Comparison of the MI-FPSE-GC–MS method with other studies

A comparison of the developed MI-FPSE-GC–MS method was carried out with other published studies, as reported in Table 2. In this study, MI-FPSE enables the extraction from a large volume of sample compared to other protocols presented in the literature (Rubirola et al., 2019; Barbosa et al., 2017; Tankiewicz et al., 2013). The use of a large volume of sample and a small volume of desorption solvent allows to achieve high enhancement factors for the target analytes. The relative recovery (RR%) values fall within the range of 80–120 % and are comparable with the RR% values of other reported methods. At the same time, the MI-FPSE-GC–MS method results in better precision (in terms of RSD% values) compared with other evaluated methods (Barbosa et al., 2017; Tankiewicz et al., 2013; Gil García et al., 2017). Another significant advantage of the proposed method is the handling simplicity, since MI-FPSE membranes are added and removed from the sample directly by using antistatic tweezers. On the other hand, MSPE and DLLME approaches require the collection of the eluent after magnetic separation and centrifugation, respectively, thus increasing the time and the cost of the analytical procedure.

3.6. Evaluation of the "green" character of the MI-FPSE-GC–MS

For the complete evaluation of the performance of the proposed MI-FPSE-GC–MS method, its "green" character was examined using ComplexGAPI index that is based on the GAC attributes (Płotka-Wasylka and Wojnowski, 2021). This metric index takes into consideration the reagents, procedures, and instrumentation that are included in the GAPI index (Płotka-Wasylka, 2018), as well as the processes that take place before analytical methodology which in this case include the fabrication of the dual sorbent-based MI-FPSE platforms. As it can be observed, the implementation of the microextraction protocol results in low consumption of organic solvents and reduced waste generation, thus complying with the GAC attributes regarding the reduction of the use of hazardous chemicals. The replacement of the chemicals with "greener" alternatives (i.e., deep eutectic solvents and natural deep eutectic solvents instead of MeOH and ACN) are future direction regarding the enhancement of the "green" character of the MI-FPSE-GC–MS method. As for the preparation of the dual sorbent-based MI-FPSE platforms, it can be observed that it shows a significant green character, since soft conditions are used, low quantity of waste is generated, low amount of energy is required, reduced occupational hazard occurs and products of high purity are obtained. Finally, the synthetic procedure is characterized by a low E-factor, thus supporting green economy. The parameter of the E-factor takes into account all what can be considered waste (for example solvents, reagents, and consumables) used per unit of mass of material made.

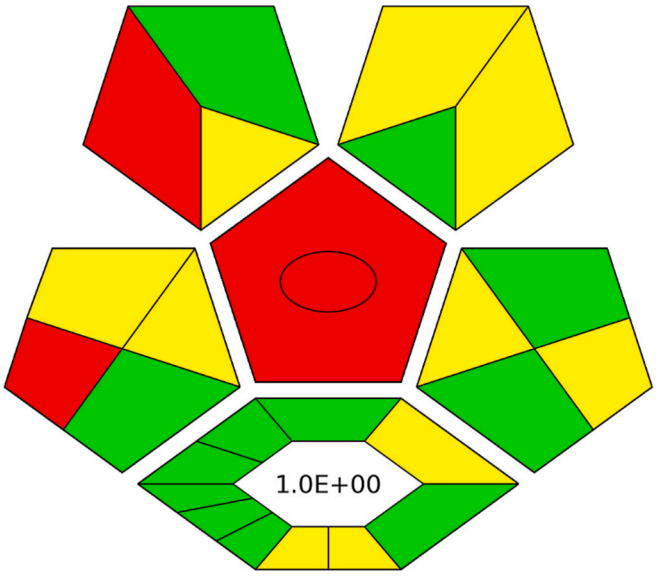

Fig. 6. ComplexGAPI pictogram for the MI-FPSE-GC–MS.

The connection between green chemistry and green economy is indeed taken into consideration in the study of Płotka-Wasylka and Wojnowski (2021), because the integration of these two concepts is needed for the implementation of the ComplexGAPI. The green economy has to be considered in order to face the environmental challenges and improve the sustainability of the green analytical processes.

The ComplexGAPI pictogram (Fig. 6) shows indeed the closeness between green chemistry and green economy, assigning corresponding scores. The processes closest to the ideal green economy are showed in green in the figure.

3.7. Determination of pesticides in water samples

Finally, the developed MI-FPSE-GC–MS method was used for the analysis of three different real water samples. River, lake, and pond

Table 3
Determination of target analytes by MI-FPSE-GC–MS in natural water samples.

Analyte	Added (ng mL^{-1})	River		Pond		Lake	
		Found (ng mL^{-1})	RR %	Found (ng mL^{-1})	RR %	Found (ng mL^{-1})	RR %
Triethyl thiophosphate	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.44 ± 0.04	87.6	0.50 ± 0.02	100.8	0.56 ± 0.01	111.9
	2.00	2.15 ± 0.03	107.6	2.01 ± 0.15	100.6	2.02 ± 0.11	101.0
Propoxur	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.46 ± 0.01	91.7	0.55 ± 0.04	110.2	0.56 ± 0.03	113.0
	2.00	2.12 ± 0.08	105.8	2.06 ± 0.11	103.0	2.01 ± 0.08	100.4
Methiocarb	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.53 ± 0.02	105.5	0.57 ± 0.05	113.9	0.57 ± 0.04	114.8
	2.00	2.19 ± 0.01	109.4	1.90 ± 0.02	94.8	1.82 ± 0.12	91.1
Thionazin	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.48 ± 0.03	96.0	0.52 ± 0.01	103.5	0.46 ± 0.06	92.1
	2.00	2.16 ± 0.03	108.1	1.84 ± 0.04	91.9	1.97 ± 0.07	98.3
Ethoprophos	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.41 ± 0.01	82.0	0.57 ± 0.03	113.4	0.50 ± 0.04	100.5
	2.00	2.09 ± 0.11	104.6	1.93 ± 0.06	96.4	1.79 ± 0.02	89.3
Phorate	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.40 ± 0.02	80.4	0.51 ± 0.02	101.9	0.49 ± 0.03	98.7
	2.00	2.18 ± 0.02	109.0	2.00 ± 0.03	99.8	1.80 ± 0.07	90.1
Trifluralin	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.38 ± 0.01	76.2	0.45 ± 0.01	89.3	0.47 ± 0.03	93.5
	2.00	2.17 ± 0.03	108.5	1.53 ± 0.01	73.6	1.55 ± 0.03	77.5
alpha HCH	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.37 ± 0.01	73.6	0.59 ± 0.05	117.4	0.50 ± 0.02	100.1
	2.00	2.00 ± 0.04	100.1	2.06 ± 0.06	103.0	1.99 ± 0.10	99.3
Sulfotep	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.50 ± 0.01	100.1	0.59 ± 0.02	118.5	0.53 ± 0.03	106.9
	2.00	2.12 ± 0.03	106.0	2.00 ± 0.05	100.1	1.96 ± 0.11	98.0
Atrazine	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.37 ± 0.02	74.2	0.45 ± 0.03	90.8	0.45 ± 0.05	89.0
	2.00	1.81 ± 0.49	90.6	1.58 ± 0.09	79.1	1.81 ± 0.04	90.6
Propazine	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.40 ± 0.02	79.0	0.45 ± 0.03	89.4	0.50 ± 0.09	99.4
	2.00	2.08 ± 0.09	103.9	1.93 ± 0.14	96.5	1.72 ± 0.03	85.9
Simazine	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.52 ± 0.02	103.3	0.59 ± 0.01	117.1	0.49 ± 0.03	98.0
	2.00	2.18 ± 0.03	108.8	2.08 ± 0.09	103.9	1.61 ± 0.04	80.5
beta-HCH	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.49 ± 0.05	97.8	0.57 ± 0.04	114.4	0.55 ± 0.01	109.5
	2.00	2.18 ± 0.02	109.1	1.86 ± 0.05	92.9	1.78 ± 0.11	89.2
gamma-HCH	0	<LOD	–	<LOD	–	0.24 ± 0.02	–
	0.50	0.47 ± 0.10	94.9	0.58 ± 0.04	116.3	0.75 ± 0.05	102.0
	2.00	2.15 ± 0.03	107.3	2.00 ± 0.13	100.0	2.25 ± 0.17	100.5
Terbuthylazine	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.44 ± 0.00	87.4	0.50 ± 0.01	99.8	0.44 ± 0.02	87.2
	2.00	2.16 ± 0.03	107.9	1.74 ± 0.05	86.9	1.53 ± 0.04	76.4
Disulfoton	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.40 ± 0.01	79.6	0.58 ± 0.01	115.7	0.54 ± 0.06	107.8
	2.00	1.99 ± 0.01	99.4	1.58 ± 0.04	78.8	1.56 ± 0.03	78.2
Sebuthylazine	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.43 ± 0.00	86.5	0.47 ± 0.01	93.6	0.42 ± 0.01	85.0
	2.00	2.17 ± 0.01	108.3	1.68 ± 0.06	83.8	1.51 ± 0.05	75.3
Metribuzin	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.35 ± 0.00	70.1	0.45 ± 0.01	90.5	0.40 ± 0.01	80.6
	2.00	2.16 ± 0.04	107.9	2.08 ± 0.02	104.1	1.79 ± 0.10	89.4
Alachlor	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.45 ± 0.01	90.6	0.56 ± 0.02	111.4	0.50 ± 0.02	99.1
	2.00	2.13 ± 0.07	106.4	1.80 ± 0.05	89.9	1.47 ± 0.02	73.3
Promethryn	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.35 ± 0.01	70.4	0.52 ± 0.02	103.1	0.49 ± 0.01	98.3
	2.00	2.18 ± 0.01	108.9	1.76 ± 0.04	88.0	1.80 ± 0.01	89.9
Parathion-methyl	0	<LOD	–	<LOD	–	<LOD	–
	1.00	1.01 ± 0.03	100.2	1.07 ± 0.02	106.7	1.03 ± 0.01	102.8
	4.00	4.17 ± 0.03	104.3	3.79 ± 0.06	94.7	3.41 ± 0.03	85.2
Fenchlorphos	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.41 ± 0.00	81.6	0.54 ± 0.01	108.0	0.49 ± 0.01	98.0
	2.00	2.18 ± 0.03	109.1	1.73 ± 0.05	86.3	1.50 ± 0.02	75.0
Terbutryn	0	<LOD	–	0.17 ± 0.01	–	<LOD	–
	0.50	0.49 ± 0.03	98.5	0.68 ± 0.01	102.0	0.46 ± 0.00	92.6
	2.00	2.15 ± 0.07	107.4	2.20 ± 0.03	101.5	1.54 ± 0.01	77.2
Fenpropimorph	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.36 ± 0.01	71.7	0.53 ± 0.01	106.1	0.43 ± 0.01	86.3
	2.00	2.00 ± 0.01	99.8	1.49 ± 0.01	74.3	1.47 ± 0.01	73.4

(*continued on next page*)

Table 3 (*continued*)

Analyte	Added (ng mL^{-1})	River		Pond		Lake	
		Found (ng mL^{-1})	RR %	Found (ng mL^{-1})	RR %	Found (ng mL^{-1})	RR %
Aldrin	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.47 ± 0.01	94.4	0.50 ± 0.01	100.4	0.48 ± 0.01	96.7
	2.00	2.06 ± 0.02	103.1	1.65 ± 0.03	82.5	1.45 ± 0.02	72.7
Chlorpyrifos	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.53 ± 0.02	106.8	0.48 ± 0.01	96.2	0.50 ± 0.01	99.4
	2.00	2.03 ± 0.01	101.4	1.47 ± 0.03	73.3	1.53 ± 0.09	76.5
Cyanazine	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.52 ± 0.03	104.8	0.50 ± 0.07	99.7	0.54 ± 0.00	108.7
	2.00	2.17 ± 0.03	108.5	1.94 ± 0.06	96.8	1.72 ± 0.16	86.1
Parathion	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.49 ± 0.03	98.2	0.59 ± 0.01	118.2	0.52 ± 0.02	103.1
	2.00	2.09 ± 0.08	104.5	1.77 ± 0.04	88.5	1.62 ± 0.11	81.0
o,p′-DDE	0	<LOD	–	<LOD	–	0.09 ± 0.00	–
	0.50	0.37 ± 0.02	73.2	0.53 ± 0.01	106.7	0.57 ± 0.00	96.0
	2.00	2.04 ± 0.01	102.1	1.69 ± 0.03	84.5	2.16 ± 0.02	103.5
o,p′-DDT	0	<LOD	–	<LOD	–	<LOD	–
	0.11	0.11 ± 0.02	100.8	0.09 ± 0.12	93.8	0.11 ± 0.01	101.1
	0.42	0.45 ± 0.02	106.1	0.39 ± 0.05	92.5	0.40 ± 0.08	95.8
Prothiofos	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.50 ± 0.00	99.8	0.48 ± 0.02	95.5	0.50 ± 0.02	99.1
	2.00	2.17 ± 0.05	108.5	1.97 ± 0.04	98.6	1.52 ± 0.10	75.9
p,p′-DDT	0	<LOD	–	<LOD	–	<LOD	–
	0.42	0.28 ± 0.01	70.1	0.29 ± 0.01	75.7	0.35 ± 0.01	89.3
	1.58	1.73 ± 0.01	109.5	1.46 ± 0.05	92.5	1.17 ± 0.01	73.9
p,p′-DDD	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.40 ± 0.06	79.4	0.41 ± 0.01	81.1	0.51 ± 0.03	101.5
	2.00	2.15 ± 0.01	107.5	1.90 ± 0.04	94.9	1.61 ± 0.04	80.5
Resmethrin	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.41 ± 0.01	82.1	0.39 ± 0.01	78.2	0.36 ± 0.01	71.5
	2.00	1.45 ± 0.01	72.4	1.53 ± 0.02	76.4	1.43 ± 0.04	71.5
Bifenthrin	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.38 ± 0.01	76.4	0.45 ± 0.01	89.8	0.37 ± 0.01	74.3
	2.00	1.46 ± 0.01	72.9	1.64 ± 0.01	81.8	1.47 ± 0.08	73.6
Methoxychlor	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.36 ± 0.01	72.4	0.37 ± 0.01	73.2	0.41 ± 0.01	82.5
	2.00	2.17 ± 0.02	108.6	1.53 ± 0.02	76.5	1.67 ± 0.04	83.3
Permethrin isomer I	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.35 ± 0.00	70.5	0.35 ± 0.01	70.8	0.38 ± 0.01	76.0
	2.00	0.76 ± 0.03	76.3	1.57 ± 0.04	78.6	0.83 ± 0.06	82.6
Permethrin isomer II	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.37 ± 0.01	70.8	0.35 ± 0.01	70.7	0.36 ± 0.04	71.4
	2.00	0.97 ± 0.14	97.3	1.64 ± 0.04	81.9	1.00 ± 0.11	100.3
Fenvalerate	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.36 ± 0.01	72.3	0.39 ± 0.01	77.9	0.47 ± 0.02	93.9
	2.00	2.08 ± 0.04	104.1	1.55 ± 0.01	77.5	2.03 ± 0.02	101.3
Cypermethrin isomer I	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.35 ± 0.01	70.8	0.39 ± 0.03	78.8	0.41 ± 0.05	82.2
	2.00	0.92 ± 0.05	91.8	1.84 ± 0.05	92.1	0.91 ± 0.16	91.3
Cypermethrin isomer II	0	<LOD	–	<LOD	–	<LOD	–
	0.50	0.41 ± 0.00	81.8	0.410.01	82.7	0.43 ± 0.01	85.9
	2.00	0.92 ± 0.04	91.9	1.85 ± 0.03	92.5	0.97 ± 0.14	97.0

water samples were collected in different districts of Vienna. All samples were analysed in three repetitions, while spiked samples at two different concentrations spiked levels (c = 0.05 ng mL^{-1} and c = 2.00 ng mL^{-1}) were also prepared to evaluate the applicability of the proposed protocol in the different samples. As shown in Table 3, percent relative recoveries were calculated for all target compounds in the three water samples and were between 70.1 % and 119.6 %. Although the method here-in proposed was developed using deionized water at 5 % *w/v* of NaCl whose characteristics in terms of salt and organic material content are less complex than the analysed samples, the good RR values found for the spiked samples, confirm that the method can be used for the determination of the target analytes in the different environmental water samples. Furthermore, given the good recovery and RSD values obtained with the proposed method, recovery correction factors were not applied. Among the examined analytes, gamma-HCH and *o,p′*-DDE were found in the lake water sample at concentrations of 0.24 and 0.09 ng mL^{-1}, respectively. Terbutryn was determined in the pond water sample at a concentration of 0.17 ng mL^{-1}, while no pesticides were detected in the river water sample.

4. Conclusions

In this research, dual sorbent-based MI-FPSE membranes namely sol-gel CW 20M–PTHF were used for the first time for multi-class extraction of pesticides in environmental surface water samples prior to their identification by GC–MS. The method exhibited good linearity over a wide concentration range, and good intra-day and inter-day repeatability results were observed. The high enhancement factor achieved by the method made it possible to obtain low LOD and LOQ values for all the target analytes. The here-in developed extraction protocol is environmentally friendly, simple, and economical. MI-FPSE membranes can be reused at least 25 times without showing substantial losses in extraction efficiency. Finally, the method was used for the analysis of environmental surface water samples such as lake, river, and pond. It

has to be highlighted, that the possibility of rapidly combining different sol-gel membranes in the laboratory to prepare dual extraction platforms shows that the extraction technique is highly flexible and adaptable for the extraction of compounds with different chemical characteristics, covering a wide range of analytes and in different research fields.

CRediT authorship contribution statement

Antonio Ferracane: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Natalia Manousi:** Conceptualization, Methodology, Investigation, Writing – original draft. **Abuzar Kabir:** Conceptualization, Data curation, Investigation, Project administration, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing, Resources. **Kenneth G. Furton:** Supervision, Project administration, Writing – review & editing, Resources. **Alice Mondello:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Peter Q. Tranchida:** Conceptualization, Writing – original draft, Writing – review & editing. **George A. Zachariadis:** Conceptualization, Investigation, Project administration, Supervision, Writing – review & editing. **Victoria F. Samanidou:** Conceptualization, Investigation, Project administration, Supervision, Writing – review & editing. **Luigi Mondello:** Conceptualization, Funding acquisition, Resources, Writing – review & editing. **Erwin Rosenberg:** Conceptualization, Investigation, Methodology, Project administration, Supervision, Writing – review & editing, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.167353.

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