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A novel strategy for preparing electrospun thin film microextraction samplers: Determining pesticides in water as proof of concept

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ABSTRACT

Thin film microextraction (TFME) greatly benefits from extractive phases with a large surface area, since this feature is paramount for rapid and effective analyte sorption. One of the techniques that can be used for preparation of TFME samplers with large extractive phase surface area is electrospinning. The traditional electrospinning, in which a polymer solution fed through a high-voltage applied nozzle is deposited to the support, may reduce the inter-sampler preparation repeatability and increase the material usage. The present study developed a new single-drop static blade electrospinning technique that can be used for homogenous coating the nano-micro sized fibrous extractive phase on the surface of stainless-steel blade, here shown using electropsun polyacrylonitrile (PAN) embedded with poly(divinylbenzene) (PDVB) nanoparticles as the extractive phase. This technique provided improved control over coating thickness while using less polymer and made it possible to fabricate ultrathin and highly uniform nanofibrous coatings in a reproducible way. The optimized static single droplet electrospinning parameters were applied voltage of 10.4 kV and a tip-to-collector distance of 8.0 cm using a slurry containing PDVB:PAN in a 1:1 ratio.

Three model pesticides (trifluralin, methyl parathion, and diazinon) were used to evaluate the extraction performance of the produced TFME samplers. Gas chromatography-mass spectrometry was then used for analysis. The electrospun PDVB-PAN samplers showed faster adsorption kinetics, with 1.7- and 5.2-fold higher slopes for methyl parathion and trifluralin, respectively, compared to bulk coated PDVB-PAN samplers in the kinetic regime of extraction. Under the same conditions, the bulk coated sampler did not show noticeable peaks for diazinon.

These results show that single-drop static blade electrospinning is a promising technique for creating high-performance TFME samplers. It provides accurate control on sorbent deposition, little material waste, with potential for use in clinical, food, and environmental matrices that require cheap and single use sample preparation devices.

1. Introduction

Solid-phase microextraction, or SPME, is a sample preparation technique with several benefits, including low solvent consumption and the ability to accommodate various sample sizes and types [1]. SPME has multiple applications in different fields, including food [2], clinical/pharmaceutical [3], and environmental [4] analysis. The design and geometry of SPME devices have changed to meet certain analytical requirements as the need for more effective and sensitive extraction techniques has grown throughout these application areas [5]. In comparison to the traditional fiber-type SPME, thin film microextraction (TFME) has a larger extractive phase volume and surface area, thus offering higher extraction recoveries, making it a significant component of the many geometries involved in SPME. This design achieves higher extraction efficiency and quicker time to equilibrium [5,6], making it popular choice.

Several extractive phases, including metal-organic frameworks [7], covalent organic frameworks [8], and carbon-based nanomaterials [9], have been investigated to enhance the efficiency of the TFME further.

The coating methods are critical for the successful development of a suitable TFME sampler as it has crucial impact on the coating's thickness, effective surface area, and coating reproducibility. These attributes

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have major impact on the coating's extraction performance. Up to date, TFME samplers have been successfully prepared using a variety of coating techniques, including spray coating [10], bar coating [11], electrospinning [12], spin coating [13], and dip coating [14]. Except electrospinning, all mentioned techniques result in deposition of bulk extractive phase on the support.

Electrospinning is used to manufacture ultra-fine materials consisting of micro or nano fibrous structures. Dissolved polymers by themselves or mixed with functional micro/nano-particles can be electrically pushed through a spinneret which results in fibrous electrospun materials [15]. Using this technique, nano/micro-fibers with a diameter between 10 nm and 10 μm are created. Several parameters critical for electrospinning can be used to alter the diameter of electrospun fibers [16]. The high surface area-to-volume ratio of electrospun materials results in the greater number of adsorption sites at the surface, available for interaction with analytes when used as an extractive phase. Thus, the amount of extracted analyte in their nano-fibrous network is higher. In addition, electrospun fibers close to the surface, benefit from radial diffusion, resulting in fast extraction kinetics. Compared to SPME or TFME probes that are not electrospun, this can lead to lower detection limits and higher method's sensitivity [17]. An additional benefit is that a variety of extractive materials, including conductive polymers, nanoparticles, and magnetic nanocomposites can be deposited within the electrospun material, increasing the versatility of the sorbents available.

As mentioned before, certain controlled parameters can be altered during the electrospinning process to get the required coating and fiber thickness with sufficient consistency. These factors include the distance between the needle and the collector, the applied voltage, the flow rate, and the viscosity of the polymer (or polymer-functional particle slurry) in the syringe. In electrospinning, the applied voltage generates an electric field between the needle and the collector, where the electrostatic force counteracts surface tension [18]. Fiber production begins when surface tension is overcome by surface charge repulsion at a critical voltage. A crucial factor in this process is viscosity; while increased viscosity promotes surface tension and helps maintain jet stability, too viscous solutions have the potential to clog the needle or dry out too quickly. The kind of polymer, molecular weight, concentration, solvent, temperature, and humidity are some of the variables that affect viscosity. Higher molecular weights, for example, result in more entangled chains, which stabilize the jet and delay early breakup. Fiber diameter is also influenced by applied voltage; greater voltages generally result in finer fibers because of increased jet acceleration. Moreover, fiber shape is affected by flow rate; high flow rates can result in uneven deposition and droplet production, while low flow rates can upset the Taylor cone [19,20]. Furthermore, the type of collector and its rotation speed have an impact on fiber alignment and deposition patterns, while the distance between the needle and collector influences the electric field strength and, consequently, fiber thickness [21].

One potential drawback of electrospinning is its extreme sensitivity to outside factors. The electrospinning conditions optimized at a given time, might not produce electrospun material or amount of material per given time interval in another time. Besides, the fiber thickness may drastically change by slight variations in variables like temperature and humidity [22,23]. As a result, rigorous control over these variables is necessary to achieve reproducible coating, making electrospinning parameters tuning more difficult. Furthermore, covering the surface in a reproducible way is the most difficult challenge when it comes to sampler preparation for microextraction because only a small amount of extractive phases are utilized.

One research area that may strongly benefit from use of TFME samplers with fast sampling while not sacrificing the analytical sensitivity is determination of pesticides in environmental and agricultural sources. Pesticides are essential in contemporary agriculture, safeguarding crops against pests, illnesses, and weeds, thereby maintaining food security. Nevertheless, the excessive and incorrect application of these chemicals can result in residues in food products and the environment, presenting significant health hazards to humans and ecosystems. Pesticide residues can result in acute poisoning, persistent health problems, and bioaccumulation within the food chain, ultimately causing long-term ecological imbalances. Consequently, the identification and detection of pesticide residues in food and environmental samples are crucial for protecting human health and preserving environmental integrity [24,25].

The use of electrospinning for preparing TFME samplers is highly preferred due to the advantages mentioned in the previous parts. Several studies have employed electrospun based TFME as a sample preparation in pesticide/insecticide determination. For instance ZIF-8 embedded in polyacrylonitrile nanofibers [26] and, polylactic acid/iron-based metal-organic framework (r-MIL-88A)/cellulose (r-MIL-88A)/cellulose) [27] TFME samplers were prepared by electrospinning and achieved very high extraction efficiency for ametrine, atrazine, metribuzine, ethofumasate and benzoylurea pesticides determined in fruit, honey, milk, apple juice and, tea samples. However, none of the studies mentioned the main difficulties that can be encountered during the sample preparation by electrospinning.

Due to its biocompatible nature, the use of PAN as a binder in SPME and TFME has been well documented. However, recent studies have shown that electrospun PAN can also serve as an extractive phase [28]. Its performance can be enhanced by the immobilization of extractive particles such as PDVB [29] and covalent organic frameworks [30], or by its partial hydrolysis [31]. Being insoluble in water and in common desorption solvents used in SPME/TFME studies makes PAN a good candidate for preparation of electrospun based TFME samplers. Moreover, micro-sized PDVB particles immobilized in polydimethylsiloxane have been reported as TFME samplers and used for pesticide extraction [32]. Thus, it can be said that PDVB nanoparticles immobilized in PAN could be a promising extractive phase for pesticides extraction.

In this study, it has been proposed to develop low-cost single-use TFME samplers with fast extraction kinetics, which can be achieved by using ultrathin coated (PDVB/PAN) electrospun materials. Inspired by coated blade spray, which is a sword like stainless steel blade coated with an extractive phase, serving both as sample preparation device and ionization source in mass spectrometry [33], a new electrospinning approach based on the electrospinning of a limited amount of coating solutions under static conditions from a sword like stainless steel blade was developed. This approach allowed to produce a controlled amount of electrospun mat with a thin layer of material, coated reproducibly. The new samplers were optimized, characterized and then evaluated in terms of their extraction performance using model pesticides.

2. Experimental

2.1. Chemicals and supplies

For synthesis of poly(divinylbenzene) (PDVB) nanoparticles divinyl benzene (DVB, 80% technical grade) was used as the monomer, aluminum oxide (activated, basic) was used as adsorbent to remove the inhibitor from DVB, hexadecane (reagent plus 99%) and sodium dodecyl sulfate (SDS, ACS reagent ≥99.0%) were used for emulsion formation, and all were procured from Sigma-Aldrich (St. Louis, MO, USA). As initiator for radical polymerization, 2–2′-azobis(2-methyl-propionitrile) (AIBN, 98%) obtained from Acros Organics (Geel, Antwerpen, Belgium) was used. Polyacrylonitrile (PAN, MW 150 KDa) and its solvent N-Dimethylformamide (DMF) were acquired from Sigma-Aldrich (St. Louis, MO, USA) and used as carrier matrix for PDVB particles during the electrospinning process. Model analytes used for evaluation of electrospun TFME samplers, diazinon, trifluralin and methyl parathion (all ≥98.0% purity), were purchased from Sigma-Aldrich (St. Louis, MO, USA). For evaluation of the effect of sample pH on extraction, buffer solutions with different pHs were prepared using disodium hydrogen phosphate (Na_2HPO_4) and potassium dihydrogen phosphate (KH_2PO_4), both purchased from ISOLAB Chemicals (Eschau, Bavaria, Germany).

For evaluation the effect of ionic strength of sample on extraction sodium chloride (NaCl) was used as sample additive and it was purchased from ISOLAB Chemicals (Eschau, Bavaria, Germany). Methanol (MeOH, LC-grade) acquired from ISOLAB Chemicals (Eschau, Bavaria, Germany) was used for preparation of pesticide stock solutions (1.0 mg/mL), dilution to intermediate stock solutions, preparing instrumental calibration solutions and to use as desorption solvent. As a carrier gas He (99.999% purity) was used in gas chromatography and it was purchased from Koyuncu (Ümraniye, İstanbul, Türkiye). Aluminum sheet was used as supporting material for TFME samplers.

2.2. Instrumentation

Before PDVB synthesis, an ultrasonic processor (SONICS VibraCell VCX500/VCX750) obtained from Sonics & Materials, Inc. (Newtown, CT, USA) was used with a setting of 500 Watt and 20 kHz to form oil in water emulsion of the pre-polymerization mixture. The synthesized PDVB nanoparticles were isolated from the matrix using a benchtop centrifuge (NüveNf200) obtained from Nüve (Ankara, Türkiye) using 5000 rpm speed. Electrospun coated TFME samplers were prepared using an electrospinning instrument (Electro-spin110) obtained from nanoWEB (Mersin, Türkiye). A plate shaker (CAT AEK-SH10) obtained from PAS Technology (Magdala, Germany) was used for any agitation purposes (including, extraction and desorption of analytes). All extraction optimization studies were conducted in purified water (18.2 MΩ.cm at 25 °C) acquired with water purification system (Milli Q Plus) procured from Millipore (Massachusetts, USA). Conductivity of water samples were measured using a conductivity meter (Cond 7110) obtained from WTW inoLab® (Weilheim, Germany).

A gas chromatograph (6890A) coupled to a mass selective detector (5973) (GC–MS) obtained from Agilent Technologies (California, USA) was used for separation and detection of the analytes. During GCMS–analysis electron impact ion source (70 eV) was used for ionization and fragmentation of the analytes. The source and quadrupole temperatures were set at 230 °C and 150 °C, respectively. The GC–MS was equipped with a 30-meter ultra-inert (5%-phenyl)-methylpolysiloxane capillary column (0.25 mm inner diameter and a 0.25 μm film thickness, Agilent Technologies, HP-5MS).

For functional group characterization, Fourier-transform infrared (FTIR) spectrometer equipped with Attenuated Total Reflectance accessory (Alpha-P) procured from Bruker (Leipzig, Germany) was used with settings of 24 scans and 4 cm^{-1} resolution. For thermal stability characterization of synthesized PDVB particles a thermogravimetric analyzer (STA 6000) obtained from Perkin Elmer (Waltham, USA) was used. The analysis was performed under N_2 atmosphere with a method heating from 30 ℃ (holds for 1 min) to 600 ℃ with 10 ℃/min hearing rate. For investigation of surface morphology of the prepared electrospun mats and the synthesized PDVB nanoparticles, a Scanning Electron Microscope (SEM, Quanta 400F) procured from FEI (Oregon, USA) was used. Before imaging, the samples were coated with Au-Pd conductive layer via sputtering.

2.3. Preparation of TFME samplers

The preparation of TFME samplers consist of several sequential steps, including PDVB synthesis, preparation of electrospinning slurry and electrospinning of the slurry to the aluminum foil surface.

For the synthesis of PDVB nanoparticles mini-emulsion polymerization described by Migenda et al. [34]. was used after slight modification of the protocol. The inhibitor, p-tert-butylcatechol, present in DVB was removed by passing some portion of DVB through activated basic alumina filled in column. Pre-polymerization mixture was prepared by addition of SDS aqueous solution (0.90 g of SDS dissolved in 12.0 mL of distilled water) into a 20-mL vial containing 0.162 mL of hexane, 3.0 mL of the inhibitor-free DVB, and 0.050 g of AIBN. The resulting mixture was mixed for 30 min at 990 rpm which was followed by an ice bath cooling. The cooled solution was homogenized with ultrasonic probe, for total of three minutes, each minute separated with a cooling break. The polymerization was then carried out in an oil bath with continuous stirring at 990 rpm overnight at 70 °C. After the reaction, the resulting milky mixture (containing the PDVB particles and reaction media) was mixed with methanol and centrifuged for 10 min at 5000 rpm to collect the resultant PDVB nanoparticles. This step was followed by washing the particles with methanol and drying them overnight at 70 °C.

The electrospinning slurry was prepared by mixing the PDVB particles in PAN solution which was prepared by dissolving 1.0 g of PAN in 9.0 g of DMF by stirring for 24 h. After that, various amounts of PDVB nanoparticles were added to PAN solution to obtain slurries with PDVB: PAN ratios of 1:4, 1:2, and 1:1, and stirred at 600 rpm for 2 h for homogenization. These mixtures were coded as M1:4, M1:2, and M1:1, respectively.

Instead of using a syringe and infusion pump to constantly feed the slurry, a sword-like shaped stainless-steel blade (0.5 mm thickness, 3 mm width and 50 mm length, the tip is in triangular geometry) was placed horizontally in front of collector plate and connected with an alligator clip to a high voltage source (Fig. 1). A droplet (10 μL) of PDVB/PAN slurry was applied to the tip of the blade. A 0.2 mm-thick aluminum foil was placed on the collector plate which was connected to the ground. By application of voltage, a 40-second electrospinning was performed, and two layers of coating were made with a 1-min drying interval. To determine the ideal parameters, the experiment was conducted under several conditions, examining voltages of 5.0, 10.0, and 15.0 kV (±0.5 kV) and distances of 8.0, 10.0, and 15.0 cm with all prepared slurries.

To fine tune the mixture composition for the best electrospinning, the polymer blends, 300 μL each, were diluted with 100, 300, and 500 μL of DMF and mixed at 600 rpm for an hour and used as coating mixtures to evaluate the coating performance. These dilutions (e.g., M1:1-D5) were designated as D1, D3, and D5, respectively. To select coatings with the most consistent distribution of PDVB nanoparticles and nanofibers SEM was used.

The TFME samplers were prepared by cutting the chosen coatings into 7.0 × 15.0 mm pieces and each was double wrapped before use.

2.4. GC–MS method

The GC-MS was utilized to separate and quantify the analytes. In the used chromatographic method, the carrier gas (He) flow rate was set at 1.2 mL/min. The injector port temperature was set at 250 °C, and 1.0 μL

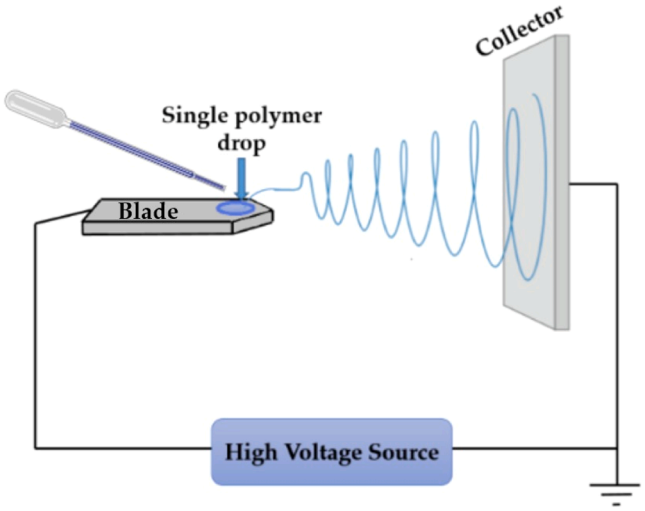


Fig. 1. Schematic representation of the single-drop static blade electrospinning process.

of the sample was injected at a split ratio of 10:1. During the GC analysis, the initial column temperature was set at 60 °C and kept at this temperature for the first five minutes, and then it was heated to 200 °C at a rate of 80 °C/min and kept at 200 °C for two minutes. The column temperature was then raised to 220 °C at 20 °C/min and held at 220 °C for 1 min. Lastly, the temperature was raised to 240 °C at 20 °C/min and held for 1 min.

The selected ion monitoring mode was used to detect the analytes with *m/z* values of 306, 109, and 152, for trifluralin, methyl parathion, and diazinon, respectively. The selected *m/z* values were the most intense ions in the mass spectrum of each analyte.

2.5. TFME studies

Extractions were performed following a three-step sample preparation protocol. For the conditioning step, the samplers were soaked in 1.5 mL of MeOH for 30 min and just before extraction, each sampler was removed from pre-conditioning solvent and surface dried by a tissue. The conditioning time was not optimized in the study and was selected based on our previous experience with various SPME and TFME samplers. Each sampler was placed in a vial containing 20.0 mL of sample, which was spiked to contain 200.0 ng/mL trifluralin and 500.0 ng/mL of methyl parathion and diazinon, and agitated at 1000 rpm for pre-determined time. At the end of the extraction, the samplers were dried again with a tissue to avoid any traces of aqueous solution entering to desorption solution. Subsequently, each sampler was placed into a vial containing 0.50 mL of MeOH for desorption and agitated at 1000 rpm for pre-determined time. The desorption volume was chosen as the smallest volume of solvent in which a sampler can be immersed completely.

It is worth mentioning that in early studies the samplers were reused. However, during immersion and removal from the vial, some damages on the extractive phase were observed. This is mainly associated with nature of the samplers as electrospun material was only physically deposited on the smooth foil surface. Thus, in this study, the samplers were treated as single use devices.

2.5.1. Optimization of the extraction/desorption conditions

In optimization studies, the desorption time profile, sample pH, and the effect of salt addition were investigated using electrospun coated M1:1-D3 samplers. The extraction was performed for 2 h with general parameters described in Section 2.5. Experiment specific parameters were as follows.

For evaluation of desorption time, 5 min, 10 min, 15 min, 20 min, and 30 min were tested. To evaluate the effect of sample pH on extraction, buffer solutions of pH 3.0, 5.0, 7.0, and 9.0 were used a sample medium where 20 min was used as desorption time. To evaluate the effect of salt addition, NaCl was added to each sample to have 0%, 5.0%, 10.0%, and 15.0% NaCl (w/v) concentration and used as the sample matrix where 20 min was used as desorption time. Each study was performed in triplicate.

2.5.2. Effect of electrospun material on extraction kinetics

TFME samplers made with the exact same slurry (M1:1-D3) but coated by dip coating (bulk polymer deposition) and electrospinning (nanofibrous polymer deposition) were evaluated and compared for their initial extraction kinetics. The extraction conditions described in Section 2.5 were used for the evaluation with extraction times of 30, 60, 120, 180, 300, and 600 s and desorption time of 20 min.

To evaluate the kinetics of extraction under unagitated conditions, the same study was repeated without using agitation during the extraction process.

2.6. Validation studies

Bottled and tap water spiked with analytes was used for method validation to evaluate the analytical performance of the new TFME samplers and developed method. The matrix-matched TFME calibration technique was used for percent recovery calculations. The water sample or ultrapure water (for matrix matched calibration) was mixed with a pH 7.0 phosphate buffer (0.10 M) in a ratio of 9:1 (v/v) to normalize the pH and ionic strength. For preparation the matrix matched calibration curves, DI water was spiked with pesticides to have 50.0, 100.0, 250.0, 500.0, 1000.0, and 1250.0 ng/mL final concentration and then diluted with buffer (9:1, v/v). Target analytes were added to tap water and commercial bottled water at three different concentration levels to have a final concentration of 100.0, 500.0, and 1000.0 ng/mL. For methyl parathion and diazinon, methyl chlorpyrifos was used as an internal standard at a final concentration of 250.0 ng/mL.

To provide thicker and more consistent sorptive coatings, the samplers used for validation were produced using the same electrospinning technique described in Section 2.3, but with five coating repetitions. The temperature and agitation settings used for extraction were the same as those used in the optimization studies. To guarantee full recovery of the analytes from the denser coating, desorption was carried out in methanol for one hour.

3. Results and discussion

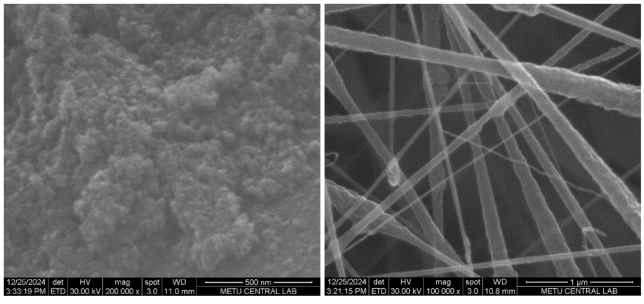
3.1. Characterization of PDVB nanoparticles

FTIR Spectroscopy, TGA, and SEM were used to characterize the prepared PDVB particles. The FTIR spectrum of PDVB nanoparticles is given in Fig. S1. The absorption resulting from C–C stretching vibrations of aromatic hydrocarbons appears in the range of 1444 and 1484 cm^{-1} and 1596 cm^{-1}, whereas C–H stretching occurs at 2919 cm^{-1}, consistent with literature regarding PDVB [29]. The thermogram for PDVB particles (Fig. S2) indicated a good thermal stability with <5% mass loss until 344 °C, consistent with literature suggesting successful synthesis of the polymer [35].

The SEM image of PDVB nanoparticles (Fig. 2a) was used to evaluate the morphology of PDVB particles. Results indicated that the PDVB particles were synthesized successfully with spherical morphology and sub-100 nm diameter, consistent with our previous study [30].

3.2. Optimization of parameters for single-drop static blade electrospinning

As first study, electrospinning parameters were evaluated using PDVB:PAN mixtures with various compositions (1:4, 1:2, 1:1; coded as M1:4, M1:2, M1:1) under different electrospinning conditions. The pictures of electrospun coating obtained under various conditions are shown in Fig. S3. It can be said that the ideal voltage–distance combination was highly sensitive to changes in the voltage and distance. While lower voltage or greater distance prevented formation of electrospun coating, higher voltage or shorter distance resulted in intense polymer deposition with bead formation. For instance, the M1:4 slurry produced



a) b)

Fig. 2. SEM image of the a) PDVB nanoparticles and b) electrospun coating prepared using M1:1-D3 polymer solution.

a coating at 9.9 kV and 5.0 cm under the conditions tried, but it was agglomerated and non-uniform. Besides, in all three mixtures, electrospinning at 15.0 kV and 10.0 cm produced unwanted droplets. As a result, 10.4 kV and 8.0 cm were chosen for additional trials since they produced the most consistent coatings among all the slurries.

Next, to further improve the coating homogeneity, 300 μL of the abovementioned PDVB:PAN slurries, were diluted with different volumes of DMF, namely, 100, 300 and 500 μL (coded with extensions of D1, D3, D5, respectively) and used for electrospinning. Then, the homogeneities of the coated surfaces were visually inspected, and the surface morphologies were investigated by SEM. The pictures of the coatings obtained after electrospinning of each slurry are given in Fig. S4. These results showed that the diameter of the coated area increased as the slurry dilution increased, with the largest coated areas being obtained for 500 μL dilutions. However, for coatings with large-coated areas it was found that the coating thickness varies from center to edges more compared to the one prepared with less diluted mixtures. Besides, for the most viscous slurry (M1:4-D1) a coating was not obtained. Considering the coating homogeneity and fabrication reproducibility, M1:1-D3 slurry (300 μL PDVB:PAN (1:1) mixture diluted with 300 μL DMF) was found to be the most appropriate for preparation of the TFME samplers. The SEM image of the electrospun mat obtained for this slurry (Fig. 2b) indicated that the average fiber diameter was 112 ± 52 nm (measured on 20 fibers). The fiber diameters were determined using ImageJ free software on the SEM image.

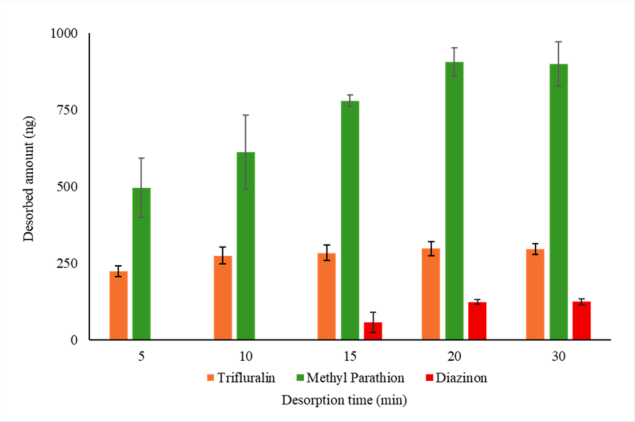
The SEM images of coatings obtained with only PAN solution and the slurries with various PDVB:PAN ratios and dilutions are shown in Supplementary Information Section Fig. S5. For all tested PDVB:PAN ratios fiber formation was observed, which proves that the new technique is not simply spraying the slurry in a bulk film. Based on the results, as dilution of the slurry increased, thinner electrospun fibers were obtained.

3.3. Optimization of the extraction conditions

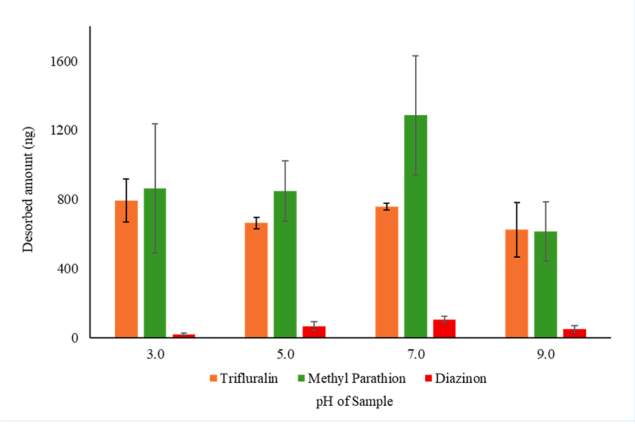
Desorption time was investigated to find the shortest time that provides complete desorption of analytes as described in Section 2.5. The obtained desorption time profile results are shown in Fig. 3a.

As can be seen from Fig. 3a, methyl parathion and diazinon desorption's were strongly effected by sampler-eluent interaction time. More specifically, both analytes showed significant increase in desorbed amounts until 20 min and then reached a plateau. Both methyl parathion and diazinon did not show a statistically significant difference (95% CL) in desorbed amounts when 20 and 30 min were compared, but there was a significant difference for comparison of 15 and 20 min. Moreover, for diazinon, at 5 and 10 min detectable desorption was not observed, which could be associated with a slower desorption of the analyte compared to the other analytes or lower instrumental sensitivity. In case of trifluralin, differently from the other two analytes, desorption maximum was achieved at shorter time, 10 min of desorption. Considering all analytes, 20 min of desorption time was chosen as optimum time and used in further studies.

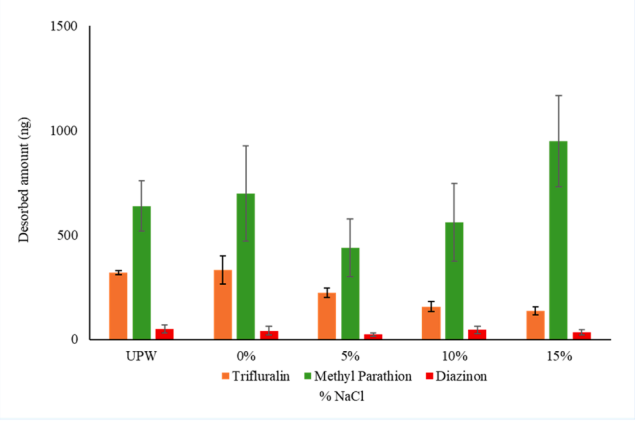
Effect of sample pH on sorption was shown in Fig. 3b At first glance it can be said that the recoveries of all analytes were affected by the medium acidity. However, relatively high deviations in the results required to perform more comprehensive evaluation using Student's test (at 95% confidence level) to compare the significance between the pHs. Comparing the results obtained for extraction at pH 3.0 and 5.0 indicated no significant difference for trifluralin and methyl parathion while the same comparison lead to a significant difference for diazinon. Comparing the results obtained at pH 5.0 and 7.0 indicated no significant difference for methyl parathion and diazinon and significant difference for trifluralin, with the opposite conclusion for pH 7.0 and 9.0 comparison. In over all, the best extraction results were obtained at pH 7.0 for all analytes. Considering that PDVB particles are neutral the main mechanism in extraction of the analyte is expected to rely on π-π



(a)



(b)



(c)

Fig. 3. Effect of a) desorption time, b) pH of the sample, and c) salt addition on extraction (Experimental conditions; analyte concentrations: 500.0 ng/mL for methyl parathion and diazinon and 200.0 ng/mL for trifluralin, volume of sample: 20.0 mL, sampling time: 120 min, desorption solvent: 0.50 mL of MeOH). UPW: ultrapure water.

interactions which is not pH dependent. Besides, PAN, used as a carrier phase in electrospinning, has dipole-dipole interaction ability with the analytes. However, the PAN, used as a carrier phase in electrospinning, has weak basic nature (the point of zero charge of the PAN is reported to be approximately 7.2 [36,37]), thus, the sampler surface is expected to be slightly positive under acidic working conditions, resulting in slight decrease in analyte extraction due to decrease in sorption contribution

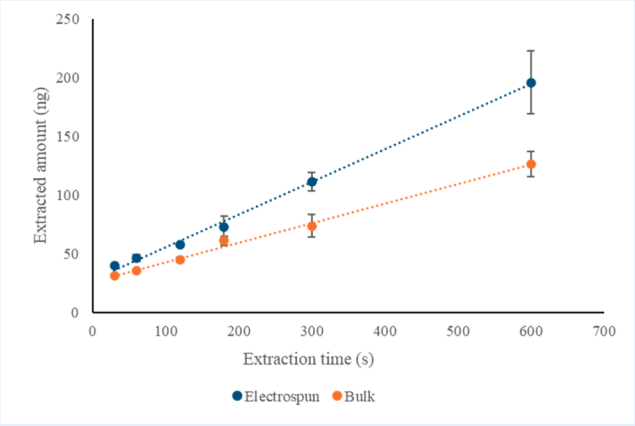
coming from PAN. Moreover, the reduction on extracted amount of methyl parathion and diazinon at pH 9.0 might be associated to their low chemical stability in basic conditions and alkaline hydrolysis [38, 39]. In overall, the results obtained here indicate that for the best extraction efficiency it would be important to adjust the pH of the sample to neutral pH. Moreover, because sample pH has strong effect on sorption, buffering the sample and matrix matched calibration solutions to a common value would be also important to avoid any problems in quantitative analysis.

To evaluate the effect of salt addition on extraction performance, the addition of NaCl (0–15% w/v) to the sample was examined in pH 7.0 buffer solution (Fig. 3c). For methyl parathion, the large deviations observed at each tested level led to non-conclusive results while for diazinon the salt addition did not have significant effect. In case of trifluralin, as salt concentration increased, a decreasing trend in sorption was observed which can be associated with low solubility of the compound leading to its precipitation from the sample, making it unavailable for extraction. In overall it can be concluded that best results are obtained under lowest ionic strength suggesting that it will be critical to have well matched matrix for TFME calibration in quantitative analysis applications. Although properly selected internal standards can be also used for such purposes, normalizing the pH and ionic strength of sample and matrix matched calibration solution to a common value is also possible solution that ensures reliable results. Measurements of pH and ion conductivity of tap water (pH= 8.01 and ion conductivity= 1250 μS) and several bottled waters (pH in a range of 7.00–8.00 and ion conductivity in a range of 151–218 μS) evidenced their variation in pH and ionic strengths. Thus, phosphate buffers with different buffer capacities were added at various ratios to tap and bottled waters to find the most appropriate matrix normalization conditions. The results showed that addition of pH 7.0 phosphate buffer (0.10 M) in a 1:9 ratio to the sample can normalize the pH and ionic strength of tap, bottled and ultrapure water to a common value (pH 7.07 ± 0.05 and 2095 ± 186 μS) and can be used for quantitative analysis.

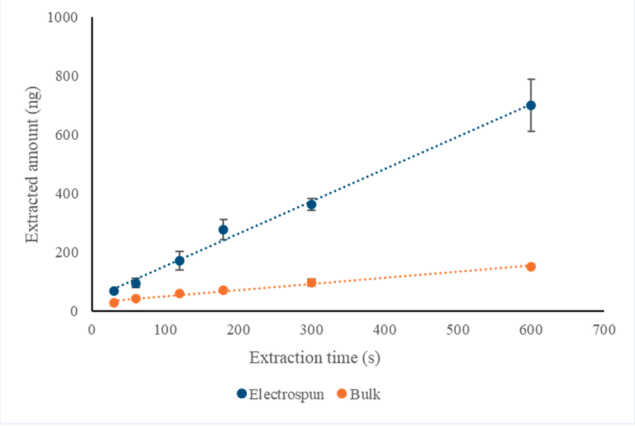
3.4. *Effect of electrospun materials on extraction kinetics*

The extraction kinetics evaluation studies were performed in a comparative manned for dip and electrospun coated samplers using extraction times of 30, 60, 120, 180, 300, and 600 s. The results of the study are shown in Fig. 4a-c.

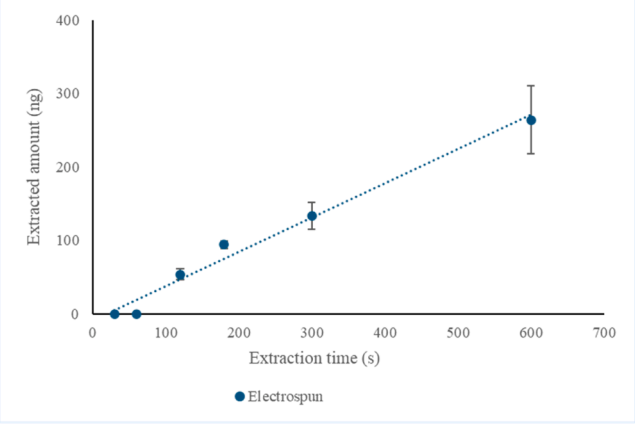
For all analytes, the electrospun nanofibrous samplers exhibited faster extraction kinetics than the bulk-coated samplers, with the difference being most noticeable for methyl parathion and diazinon. Since under tested conditions a linear correlation between extraction time and amounts of analyte extracted was obtained, it can be concluded that the extraction is within linear regime which is described as extraction time that results in extracted amount of 50% or less of extracted amounts of analyte at equilibrium. Thus, the ratio of slopes of linear regression equations obtained for electrospun and bulk coated samplers can be used for comparison of extraction efficiency enhancement. The slope ratios for trifluralin and methyl parathion were found to be 1.7 and 5.2, respectively, while for diazinon could not be calculated as diazinon did not show any noticeable peaks for bulk coated samplers under investigated extraction conditions. This could be because of low instrumental sensitivity, restricted affinity, or a slower extraction rate. The overall observed enhancement of electrospun coated samplers may be associated to the larger surface area-to-volume ratio of these samplers, which offers more adsorption sites available for analyte interaction. Moreover, the impact of radial diffusion which is effective in samplers with diameters <25 μm could also contribute to the electrospun coated samplers' improved kinetics [40] as each electrospun fiber on the surface of the sampler may act as a separate micro-sampler with diameters resulting in radial diffusion. Thus, the performance advantages of the suggested design can be confirmed for nanofibrous samplers, which enable the achievement of analyte quantities significantly higher than those obtained with bulk samplers.



(a)



(b)



(c)

Fig. 4. Comparison of initial extraction time profile for a) trifluralin, b) methyl parathion, and c) diazinon using electrospun and bulk-coated samplers (Extraction conditions; analyte concentrations: 500.0 ng/mL for methyl parathion and diazinon and 200.0 ng/mL for trifluralin, volume of sample: 20.0 mL. Desorption conditions; desorption solvent: 0.50 mL of MeOH, desorption time: 20 min; Extraction and desorption agitation: 1000 rpm). Note that in 'Fig. 4c' the bulk samplers did not provide quantifiable signal.

The kinetic studies performed under agitated conditions were also repeated under static conditions (no sample agitation performed). This was performed to see if the fast extraction kinetics observed for the nanofibrous structure under agitation conditions is also effective under

unstirred conditions, since many on-site studies (e.g. time weighted average monitoring with retracted devices) may need sampling under static conditions. The results obtained for this evaluation are shown in Fig. 5a-c. In the figure, the extraction results obtained under agitation conditions were also included for easy comparison.

Similar to results obtained under agitation conditions, a linear extraction trend was also observed, suggesting that the extraction is in linear regime of the extraction time. Moreover, it can be seen that with agitation conditions improved extraction uptake rate can be obtained and it is critical to perform agitation for a reasonable extraction efficiency in short time. Interestingly, for trifluralin and diazinon, higher amount of analytes were extracted in static conditions in extraction times <120 and 180 s, respectively. Besides, for diazinon which did not show any noticeable peaks for bulk-coated samplers (Fig. 4c) under agitation extraction conditions, with electrospun coated samplers, detectable signal was obtained even at the lowest tested time at static conditions.

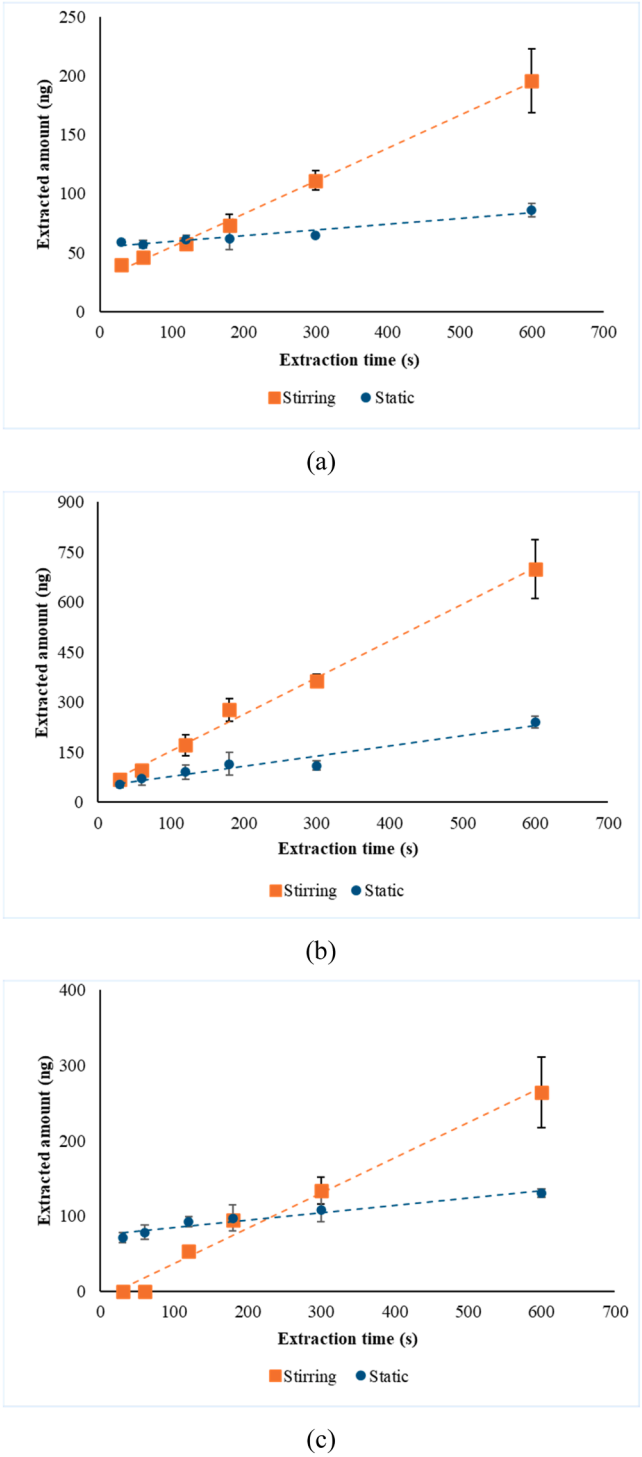


Fig. 5. Comparison of initial extraction time profile for a) trifluralin, b) methyl parathion, and c) diazinon using electrospun coated sampler under static and stirring conditions (Extraction conditions; analyte concentrations: 500.0 ng/mL for methyl parathion and diazinon and 200.0 ng/mL for trifluralin, volume of sample: 20.0 mL. Desorption conditions; desorption solvent: 0.50 mL of MeOH, desorption time: 20 min, desorption agitation: 1000 rpm).

3.5. Validation studies

Validation of the proposed TFME-GC–MS method was performed using spiked tap and bottled water samples. The percent recoveries were calculated using matrix-matched TFME calibration with $1/X^2$ weighing (calibration equations provided in Table S1).

For recovery assessment of the method, three levels (low, mid and high points; 100.0, 500.0 and 1000.0 ng/mL) of analytes were spiked to tap and commercial bottled water samples. Recovery (%) values for the three target analytes (methyl parathion, diazinon, and trifluralin) were given in Table 1. For diazinon, both in tap and bottled water, at mid and high levels good recoveries have been achieved. In case of methyl parathion, in tap water, similar to diazinon the recoveries were close to 100% while more deviation was obtained in bottled water. Trifluralin on the other hand showed the highest bias at all tested levels and waters, with more reasonable results obtained at the highest tested spike level. In the comparison of reproducibility at low, mid, and high point levels, the percentage relative standard deviations (RSDs), excluding trifluralin, were generally lower than 20% (Table 1). The limited solubility of trifluralin (indicated also by its high logP value), might be the reason for the observed high relative standard deviations. On the other hand, the low RSD (%) values obtained for other analytes indicate that the developed method performs consistently across both matrices, and method precision is at an acceptable level.

Besides, the method's sensitivity was evaluated in terms of analytical sensitivity which is defined as the ratio of the slope of the calibration curve (here matrix matched TFME calibration) to standard deviation obtained at a given concentration. Based on this evaluation, the analytical sensitivity for trifluralin was 0.022 and 0.0054; for methyl parathion, 0.015 and 0.0038; and for diazinon, 0.048 and 0.0048 at 100.0 and 1000.0 ng/mL spike levels, respectively. These results indicate that at low concentration the method sensitivity is lower with the best value obtained for diazinon, and at higher concentrations analytical sensitivity for all analytes improves with values in similar range.

Overall, the validation results show that the technique maintains good linearity (Table S1) and precision throughout the tested range but still needs further improvements for accurate determinations of organophosphorus pesticides in water samples. This can be achieved by reconstitution of the desorption solution in a smaller volume before GC–MS analysis or using isotopologues of the analytes as internal standard in the samples and matrix matched calibrations.

4. Conclusion

In this study, new TFME samplers were generated by embedding PDVB nanoparticles within a PAN matrix using a single-drop static blade electrospinning approach. Unlike conventional syringe-based electrospinning, this novel coating technique made possible the production of consistent and ultrathin fibrous coatings. The most consistent coatings were obtained with a slurry containing PDVB:PAN ratio of 1:1 which was further diluted 1:1 with DMF under ideal circumstances (10.4 kV, 8.0 cm).

The proof-of-the concept evaluations performed using three pesticides (methyl parathion, diazinon, and trifluralin) demonstrated that the

Table 1
Recovery and reproducibility results for spiked tap water and bottled water samples.

	Analyte	Recovery (%) (n = 3)			RSD (%) (n = 3)		
		100.0 (ng/mL)	500.0 (ng/mL)	1000.0 (ng/mL)	100.0 (ng/mL)	500.0 (ng/mL)	1000.0 (ng/mL)
Tap	Methyl parathion	76	99	107	14.0	18.8	22.6
Water	Diazinon	136	104	118	13.7	19.5	13.5
	Trifluralin	129	49	84	27.3	68.9	21.0
Bottled	Methyl parathion	47	86	56	7.5	15.0	19.1
Water	Diazinon	129	121	84	2.8	11.4	18.9
	Trifluralin	191	131	85	2.8	17.9	16.3

samplers provided reliable intra-device repeatability. Most importantly, the extraction efficiency of the electrospun coated samplers was higher than that of the bulk-coated counterparts when compared under extraction time fitting within linear regime of the extraction time. In addition, although stirring speeded up the extraction rates, quantifiable analyte recovery was still possible without agitation, suggesting that the samplers would be useful for on-site sampling when agitation is not possible.

The investigations performed in different pH and ionic strength conditions with the selected analytes showed that the samplers perform the best at neutral pHs and it would be critical to use internal standard or normalize the sample and matrix-matched calibration solutions to common conditions (i.e. pH and ionic strength). Finally, the preliminary validation studies indicated promising results, but further improvement in method's figures of merits is needed especially for ultra-trace analysis.

Because of limited coating stability, the new sampler has been designed as a single use device, which may appear economically unfavorable. However, from the practical viewpoint, preparation of the sampler is simple and low cost, and can be readily adapted in laboratories having high voltage source, thus, offsetting the drawback associated with its single use nature.

CRediT authorship contribution statement

Alper Şahin: Writing – original draft, Investigation, Formal analysis, Data curation. **Yeliz Akpınar:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Maksut Samedinov:** Validation. **Ezel Boyaci:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they possess no obvious conflicting financial interests or personal ties that may have influenced the work presented in this study.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jcoa.2026.100344.

Data availability

Data will be made available on request.

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