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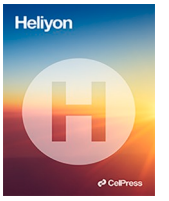

Research article

New fabric phase sorptive extraction for nondestructive analysis of heritage textile samples

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ABSTRACT

Several types of pesticides used in museum collections over time become dangerous for people who may handle textile articles treated with such substances. In the case of the analysis of ancient, modern, and contemporary textile materials, it is particularly important to keep the artifacts intact, as they cannot be replaced. The need to use micro- or nondestructive techniques led to the development of methods such as solid-phase microextraction (SPME), liquid–liquid dispersive microextraction (DLLME), and single-droplet microextraction (SDME). In this paper is described an optimized extraction method of three pesticides (malathion, methoxychlor, and permethrin) by creating a non-destructive solid phase extraction system on a textile support, abbreviated FPSE – 100 % cotton fabric coated with a sol-gel solution prepared from a polymer (PEG or PDMS). To obtain a suitable FPSE, the following parameters were evaluated: polymer selection (individual or mixture of polymers), acid catalyst (trifluoroacetic acid, acetic acid and hydrochloride acid), amount of polymer (1.0 g, 2.5 g or 5.0 g), polymerization time (30 min, 120 min and 240 min), ultrasonic bath temperature (40 °C and 70 °C), and type of bath to obtain the sol-gel (ultrasonic bath, water bath with stirring and mechanical stirrer). To complete the FPSE optimization, the influence of pesticide extraction time on FPSE and desorption from FPSE in ethyl acetate was also assessed.

The pesticides extraction yields obtained for the laboratory textile samples are in the range of 52.7 %–128.0 %. The technique proposed in the manuscript proved to be effective as a nondestructive tool for evaluating and quantifying the presence of pesticides in textile museum collections. The approach described here reduces heritage object damage due to sampling compared to methods commonly employed and may represent a starting point for future research.

1. Introduction

Several types of pesticides or fumigants used in museum collections over time become dangerous for people who may handle textile articles treated with such substances [1]. In the case of the analysis of ancient, modern, and contemporary textile materials, it is particularly important to keep the artifacts intact, as they cannot be replaced.

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Advanced analytical methods and techniques are an essential choice in the field of cultural heritage, as they provide the means to investigate textile collections [2,3]. The determination of organic pesticides can be problematic due to their volatility, so the election of the analysis method must be made considering this aspect. To determine the presence of pesticides in the samples to be analyzed, these must go through processes such as extraction, enrichment, isolation, identification, and quantification [4].

Gas chromatography is one of the analytical techniques used for the separation of volatile organic components that may be present in modern and contemporary textile art objects [5–8]. Mass spectrometry (MS) is also a widely used technique for pesticide detection due to its good sensitivity and capability to provide structural information about the analyzed compounds. Although there are many extraction techniques, such as liquid–liquid extraction (LLE) [9], solid–liquid extraction (SLE), supercritical fluid extraction (SFE) [10], and QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) [11], due to their destructive nature, they cannot be used on heritage samples unless other options cannot be implemented.

The need to use micro- or nondestructive techniques led to the development of methods such as solid-phase microextraction (SPME) [12–16], liquid–liquid dispersive microextraction (DLLME) [17], single-droplet microextraction (SDME) [18], and more recently, a new type of extraction was developed by Kabir and Furton [19], known as fabric phase sorptive extraction (FPSE).

Fabric phase sorptive extraction consists of five main components:

a. The substrate – cotton, polyester, or other types of textile material.
b. The sol-gel solution consists of one or more inorganic/organic modified sol-gel precursors and is used for creating the sol-gel sol coating on the surface of the substrate.
c. An inorganic/organic active sol-gel polymer.
d. A compatible solvent system.
e. An acid catalyst and water for hydrolysis.

FPSE procedure is based on the direct contact of the FPSE with the sample, and is considered to be the only micro-extraction technique that:

➢ analyzes the surface chemistry of the fabric substrate to realize the overall selectivity and extraction efficiency of an FPSE membrane.
➢ offers the possibility to use a wide variety of adsorbents while maintaining extraction performance characteristics such as robustness, specificity, and efficiency [20].

Application of FPSE technique is presented in Table 1.

According to a review published by Kabir A. and Samanidou V. [20], 66 papers were published from 2014 to 2020, with an increased trend of publication of these papers, as can be seen in Fig. 1 updated with dates up to 2022.

In this paper, is presented a new fabric phase sorptive extraction (FPSE) method for the nondestructive analysis of three types of pesticides (malathion, methoxychlor and permethrin) that can be present in modern and contemporary textile objects. The proposed system is significant, as it focuses on assessing the risks to human health posed by the formerly widespread practice of pesticide use by developing and optimizing an innovative non-destructive extraction method, which can be used to assess pesticides from museum textile objects. The separation and detection methods are optimized, validated and described in another work [26].

2. Materials and methods

To obtain an analytic system for determination of malathion, methoxychlor and permethrin, a GC-MS method was coupled with a fabric phase sorptive extraction. The equipment used was an Agilent 6890 N gas chromatograph with MS 5973 mass spectrometric detector, ZB-5MSi column from Phenomenex, and the substances were PESTANAL® analytical grade. GC-MS operating parameters are presented in Table 2.

Table 1
FPSE application.

Technique	Substrate	Sol-Gel	Sample	Reference
FPSE-HPLC-UV	Cellulose	PEG	Tap water Substituted phenols	[21]
FPSE-HPLC-FLD	Cellulose	PTHF	Hospital wastewater Estrogen	[22]
FPSE-HS-GC-MS	Glass fibre	PDMDPS	Ambient air Sex pheromone	[20]
FDSE-FI-FAAS	Polyester	PDMDPS	River water Toxic metals	[23]
Stir-FPSE-UPLCDAD	Cellulose	PEG	River water Herbicides	[24]
SE/GC-MS	Cellulose	CW/PTHF/PDMS	Vegetable samples Organophosphorus pesticides	[25]

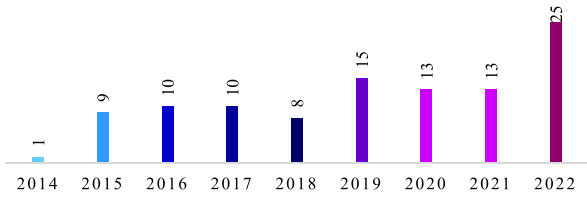

Fig. 1. Graph adapted from Kabir A. and Samanidou V [20].

To obtain the FPSE, the experiments are presented in the following way:

2.1 – FPSE development: 4 possible polymers are selected, and a first preparation method is used, based on the individual polymers or the mixture of them, resulting in 14 variants of FPSE.
2.2 – FPSE optimization: in this step, 2 variants of FPSE out of the 14 proposed in phase 2.1 are selected. Also, the preparation parameters of the FPSE method proposed in phase 2.1 are optimized.

2.1. FPSE development

2.1.1. Fabric preparation

The fabric used as a substrate was 100 % cotton. This is cut into 10 cm × 10 cm squares, which are subjected to the following treatments:

1 Wash with distilled water
2. Treatment with 1 M sodium hydroxide solution for 1 h in an ultrasonic bath at room temperature
3. Wash with distilled water
4. Treatment with 0.1 M hydrochloric acid solution for 1 h in an ultrasonic bath at room temperature
5. Rinse with distilled water.
6. Dry overnight at room temperature and store in an airtight container.

2.1.2. Sol-gel preparation

The reagents used are *polymers*: polyethylene glycol (PEG), dimethylpolysiloxane (PDMS), polylactic acid (PLA) and ethyl cellulose (EC), *trimethoxymethylsilane* (MTMS), *solvent*: methylene chloride: acetone (50/50: V/V), and *acid*: trifluoroacetic acid 5 % water (TFA 5 %).

1. In a reaction vessel, 2.5 g of polymer (individual or mixture), 2.5 mL of MTMS, 5 mL of solvent and 1.0 mL of 5 % TFA were added.

The variants obtained (Table 3) consist of varying the type of polymer used, either individually or by mixing the polymers:

- version with one polymer: 2.5 g
- version with two polymers: 1.25 g/polymer
- version with three polymers: 0.83 g/polymer
- version with four polymers: 0.63 g/polymer

2. The reaction vessel was shaken vigorously and then kept in an ultrasonic bath at 70 °C for 30 min and vortexed for 3 min at a speed of 2500 rpm.

Table 2
GC-MS operating parameters.

Technique	Parameters
GC	Injection volume: 1 μL Gas flow: 1.2 mL/min Injector temperature: 300 °C Auxiliar temperature: 300 °C Oven: from 130 °C to 280 °C with 15 °C/min; hold 10 min at 280 °C
MS	SIM method Malathion ions: 93, 125, 173 Methoxychlor ions: 152, 227, 228 Permethrin ions: 163, 165, 183 Dwell: 50

Table 3
Sol-gel variants.

One polymer	PEG		PDMS		PLA	EC
Two polymers	PEG/PDMS	PEG/PLA	PEG/EC	PDMS/PLA	PDMS/EC	PLA/EC
Three polymers	PEG/PDMS/PLA		PEG/PDMS/EC		PDMS/PLA/EC	
Four polymers	PEG/PDMS/PLA/EC					

3. The reaction vessel is then stirred for 15 min at room temperature at a speed of 450 rpm using a mechanical stirrer, and after this, the obtained mixture is centrifuged for 5 min at a speed of 5000 rpm at 20 °C, and the supernatant is collected. If not used at once, it can be stored in an airtight dark container.

2.1.3. Final sol-gel fabric preparation (FPSE)

1. The textile support obtained in step 2.1.1 is cut into squares of 5 cm × 5 cm and immersed in the solution prepared in step 2.1.2 for 2 h at room temperature.
2. The extraction membrane thus obtained was dried for 24 h at 50 °C in an oven with 20 % ventilation in a standard atmosphere.
3. The obtained FPSE was washed with a solution of methylene chloride: acetone (50/50:V/V) and dried for 1 h at 50 °C in an oven with 20 % ventilation in a standard atmosphere. If not used at once, FPSE can be stored in an airtight dark container.

An important aspect to mention is that to obtain the extraction membrane, a thermostatic oven generally available in most laboratories and a standard atmosphere was used, compared to the methods found in the literature, where the drying is carried out in a thermostatic oven with an inert atmosphere – in the existing works, helium is used, an expensive inert gas with ever-increasing prices.

2.1.4. Fabric phase sorptive extraction of pesticides

One square of 1 cm × 1 cm FPSE is immersed for 10 s in a solution of methanol: acetonitrile (V:V = 1:1) to activate the surface. The FPSE was then introduced into 1 mL of 100 ppm pesticide mix solution and kept for 30 min at room temperature.

After 30 min, the FPSE was removed, left for 1 min at room temperature and then placed in 2 mL of ethyl acetate for pesticide extraction. The desorption was performed on a mechanical shaker at 500 rpm for 1 h at room temperature. After the desorption time is over, the vessel with FPSE is left for 10 min at room temperature, and then the solution is injected into the chromatographic system coupled with a mass spectrometer detector.

2.2. FPSE optimization

To obtain a suitable FPSE, 2 variants from the 14 proposed in section 2.1 **FPSE development** are selected* and the following parameters are varied: the acid catalyst, amount of polymer, polymerization time, ultrasonic bath temperature, and type of stirring to obtain the sol-gel. To obtain a shorter preparation method, the influence of the last steps for sol-gel preparation is verified. To complete the FPSE optimization, the influence of pesticide extraction time on FPSE and desorption from FPSE in ethyl acetate and extraction from textile samples are modified.

*The variants selected are prepared of one polymer each: PEG and PDMS.

2.2.1. Influence of the acid catalyst, amount of polymer, polymerization time, bath temperature and type of bath used

All the steps for FPSE optimization are the same as for FPSE development. Each varied parameter is conducted one at a time for a better understanding of their influence on pesticide extraction.

First, to see the influence of the ***acid catalyst*** on the extraction system, three variants were prepared: trifluoroacetic acid 5 % water (TFA), hydrochloric acid 5 % water (HCl), and glacial acetic acid 5 % water (AA). Second, the influence of the ***amount of polymer*** on the extraction system is found using three variants with 1 g, 2.5 g, and 5 g of polymer.

The influence of ***polymerization time*** is evaluated by keeping the textile support in the polymeric solution for 30, 120, and 240 min.

The last two steps are the ***bath temperature***, which is set at 70 °C or 40 °C, and the ***type of bath***, evaluated for the use of an ultrasonic bath (UB), magnetic stirrer (MS) and water bath with stirring (WB).

2.2.2. Influence of the last steps of the sol-gel preparation

The last steps of the sol-gel preparation consisted of stirring the reaction vessel for 15 min at room temperature at a speed of 450 rpm using a mechanical stirrer, and after this, the obtained mixture was centrifuged for 5 min at a speed of 5000 rpm at 20 °C, and the supernatant was collected. Because polymer solutions are clear and have no visible undissolved polymer and to evaluate if these steps influence the results, two variants of FPSE are obtained: one that includes these stages (noted with "PEG or PDMS-long") and another without (them) these ones (noted with "PEG or PDMS-short).

2.2.3. Influence of pesticide extraction time on FPSE and desorption time from FPSE in ethyl acetate

At this point, an optimized FPSE is obtained. Furthermore, the activated FPSE was introduced into 1 mL of 100 ppm pesticide mix solution and kept for 30, 60, and 120 min at room temperature. Each variant was then removed and left for 1 min at room temperature

and placed in 2 mL of ethyl acetate for pesticide desorption. The desorption was conducted on a mechanical shaker at 500 rpm for 30, 60, and 120 min at room temperature.

After the end of the extraction-desorption time, the vessel with FPSE was left for 10 min at room temperature, and the solution was injected into the chromatographic system. The samples were coded accordingly:

PEG or PDMS 30-30: 30 min in pesticide mix +30 min in ethyl acetate
PEG or PDMS 30–60: 30 min in pesticide mix +60 min in ethyl acetate
PEG or PDMS 30–120: 30 min in pesticide mix +120 min in ethyl acetate
PEG or PDMS 60-30: 60 min in pesticide mix +30 min in ethyl acetate
PEG or PDMS 60-60: 60 min in pesticide mix +60 min in ethyl acetate
PEG or PDMS 60–120: 60 min in pesticide mix +120 min in ethyl acetate
PEG or PDMS 120-30: 120 min in pesticide mix +30 min in ethyl acetate
PEG or PDMS 120-60: 120 min in pesticide mix +60 min in ethyl acetate
PEG or PDMS 120-120: 120 min in pesticide mix +120 min in ethyl acetate

2.2.4. Extraction from textile samples

Four types of fabrics were used: 100 % wool, 100 % cotton, 50%–50 % cotton/polyester and 50%–50 % cotton/polyamide (Table 4).

A 1 cm × 1 cm square FPSE from each sample was immersed for 10 s in a solution of methanol:acetonitrile (V:V = 1:1) to activate the surface. The extraction of pesticides from textile materials is conducted in two ways:

1. FPSE is placed on the textile materials treated with a theoretical solution of 1.5 ppm pesticide mix and kept for 60 min in the case of PEG-FPSE and 120 min in the case of PDMS-FPSE at room temperature.
2. A drop of 500 μL of distilled water is placed on the textile materials treated with a theoretical solution of 1.5 ppm pesticide mix, and FPSE is placed immediately on top of it and held for 60 min in the case of PEG-FPSE and 120 min in the case of PDMS-FPSE at room temperature.

After the extraction time, the FPSEs were placed in 2 mL of ethyl acetate for pesticide desorption. The desorption was performed on a mechanical shaker at 500 rpm for 120 min at room temperature.

After the desorption time is over, the vessel with FPSE is left for 10 min at room temperature, and then the solution is injected into the chromatographic system.

3. Results and discussion

Before presenting the results, we note that the values shown are mean values and not individual values. Each experiment was carried out 5 times.

3.1. FPSE development

To evaluate the obtained results, the areas of the chromatographic peaks corresponding to each analyte of interest were compared (Fig. 2).

Regarding the number of polymers, the areas obtained for the variants with a single polymer are higher than those obtained in the case of using a mixture of polymers for all analytes. If referring to the type of polymer, from the graphical representation of the results (Fig. 1), the variants with PEG and PDMS present the highest values for all the analytes of interest. This can be explained by the fact that during the polycondensation the selected polymers react with the available hydroxyl groups of the cellulosic substrate, creating covalent bonded sol-gel coating uniformly distributed through the matrix with high chemical stability and active sites for analyte extraction. The better results obtained for PEG and PDMS may be attributed to the ability to form intermolecular hydrogen bonds, thus facilitating the possible formation of an extended hydrogen-bonded structure between the fabric phase sorptive extraction and the three analytes of interests.

Considering these results, dimethylpolysiloxane (PDMS) and polyethylene glycol (PEG) polymers will be used to optimize the fabric phase sorptive extraction method.

Table 4
Textile fabric samples.

Composition	Sample code
100 % Cotton	CO
100 % Wool	WO
50 % Cotton – 50 % Polyester	CO/PES
50 % Cotton – 50 % Polyamide	CO/PA

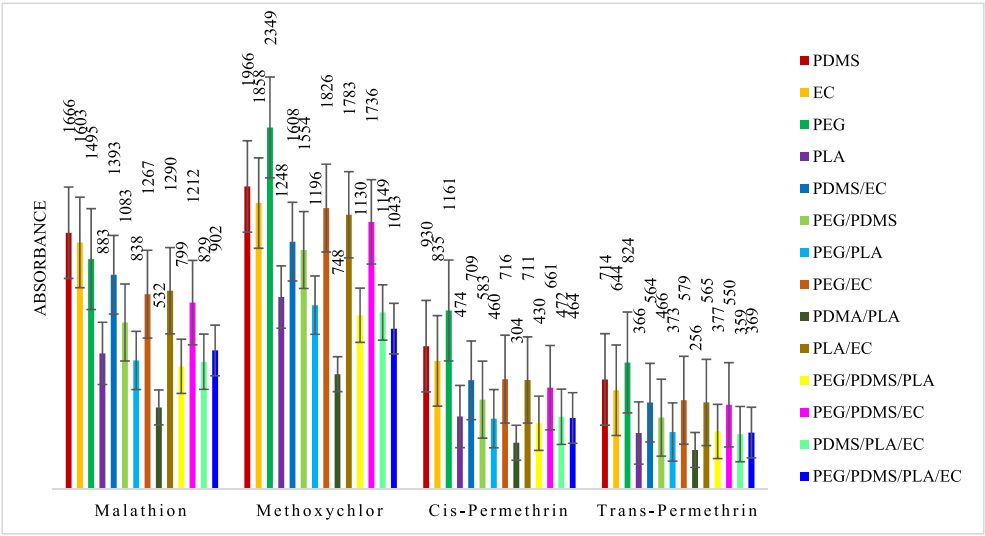

Fig. 2. Graphic representation of the FPSE development.

3.2. FPSE optimization

3.2.1. Influence of the acid catalyst, amount of polymer, polymerization time, bath temperature and type of bath

Influence of the acid catalyst: For the evaluation of this parameter, an observation must be made: the version with hydrochloric acid and PEG could not be analyzed. After the polymerization and drying stage, the FPSE obtained could not be removed from the Petri dish in which it was polymerized, showing disintegration of the textile support (Fig. 3).

For the rest of the samples, the results are presented in Fig. 4.

Comparing the results obtained for both PEG and PDMS polymers, it can be seen that the use of trifluoroacetic acid results in obtaining the largest chromatographic peak areas for malathion, methoxychlor and *cis*-permethrin. Trifluoroacetic acid (TFA) is the strongest acid compared to the other two acids used, acetic acid (AA) and hydrochloric acid (HCl). The highly electronegative fluorine atoms and the electron-withdrawing nature of the trifluoromethyl group allow for greater acidity, leading to weak oxygen-hydrogen bonding and a stable anionic conjugate base of the analytes of interest. This could explain the largest areas obtained in the case of TFA use, compared with AA and HCl.

For *trans*-permethrin, the use of acetic acid leads to slightly increased surface areas compared to the other acid catalysts, but due to the insignificant difference in results, trifluoroacetic acid will be used for the next steps of the optimization process.

A graphic representation of the result obtained for ***the influence of the amount of polymer*** is presented in Fig. 5.

As seen both in the case of PEG and PDMS, the amount of 2.5 g of polymer leads to higher values of chromatographic peak area. An interpretation of these results can be attributed to the fact that, in the case of using the amount of 1.0 g of polymer, the surface of the active extraction sites is not sufficiently extensive to obtain an efficient extraction, and on the other hand, in the case of using the amount of 5.0 g of polymer, the results could be explained by an unavailability of the extraction sites of the analytes of interest.

The results achieved for the ***influence of the polymerization time*** are presented in Fig. 6.

As seen in Fig. 6a), in the case of *cis*-permethrin, a polymerization time of 240 min results in larger areas compared to the other two variants. However, considering the area values obtained for the rest of the compounds, both in the case of using the PEG polymer and PDMS polymer, a time of 30 min will be used for the polymerization of the sol-gel on the textile support.

A graphic representation of the ***bath temperature*** results is shown in Fig. 7.

The obtained results do not show significant differences in terms of the temperature values used for the sol-gel preparation, which means that the formation of the sol-gel network is not influenced by them. For the PEG polymer slightly larger areas are obtained in the

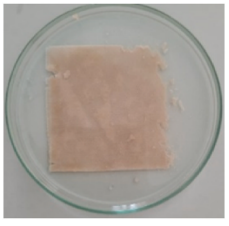

Fig. 3. PEG-HCl sample.

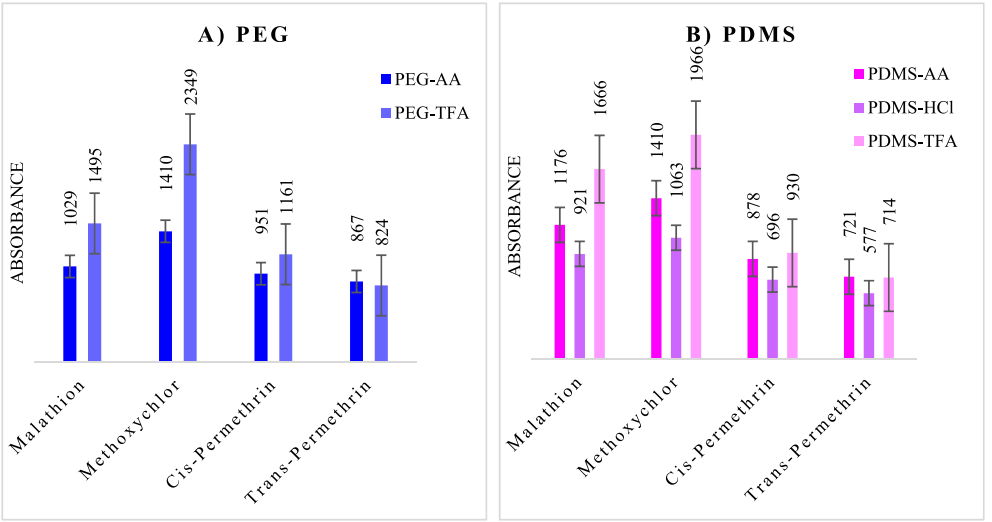

Fig. 4. Graphic representation of the results obtained for the influence of the acid catalyst: a) PEG-FPSE, b) PDMS-FPSE.

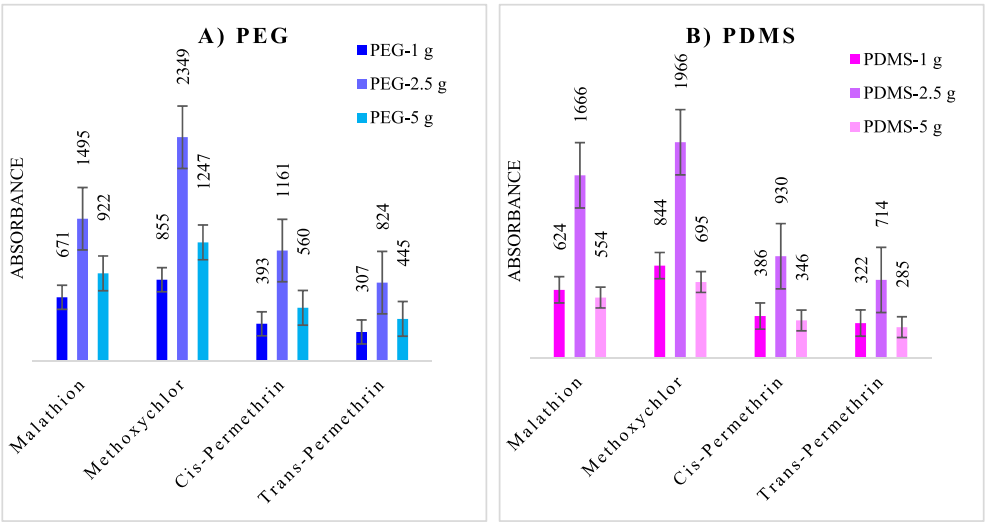

Fig. 5. Graphic representation of the results obtained for the influence of the amount of polymer: a) PEG-FPSE, b) PDMS-FPSE.

case of the temperature of 70 °C for malathion and methoxychlor and 40 °C for permethrin, both isomers. In the case of the PDMS polymer, the temperature of 70 °C leads to moderately higher results compared to those for the temperature of 40 °C. Considering the above, the temperature of 70 °C will be used.

The following parameter is the ***type of bath*** used to obtain the sol gel, and the results are shown in Fig. 8.

The use of a water bath with stirring leads to the lowest area values, while the ultrasonic bath gives the highest area values. These results can be expected since ultrasonication acts as an external stimulus to higher monomer concentration in polymer particles. Considering the results obtained, an ultrasonic bath will be used for both PEG and PDMS FPSE.

3.2.2. Influence of the last steps of the sol-gel preparation

No noticeable differences are obtained between the "short" or "long" method for the preparation of sol-gel; thus, the final formula will not include 15 min of stirring at room temperature at a speed of 450 rpm using a mechanical stirrer and centrifugation for 5 min at a speed of 5000 rpm at 20 °C (see Fig. 9).

3.2.3. Influence of pesticide extraction time on FPSE and desorption time from FPSE in ethyl acetate

Graphic representation of the results obtained for evaluating the influence of pesticide extraction time on FPSE and desorption time from FPSE in ethyl acetate is shown in Fig. 10 (PEG-FPSE) and Fig. 11 (PDMS-FPSE).

As seen in Fig. 10, the best extraction variant in the case of PEG-FPSE is the one in which the extraction of pesticides by FPSE is 60

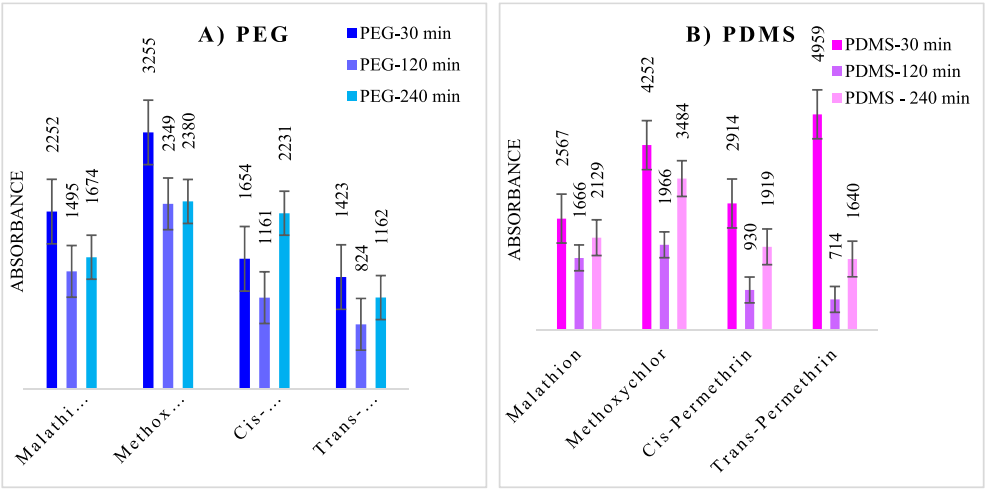

Fig. 6. Graphic representation of the results obtained for the influence of the polymerization time: a) PEG-FPSE, b) PDMS-FPSE.

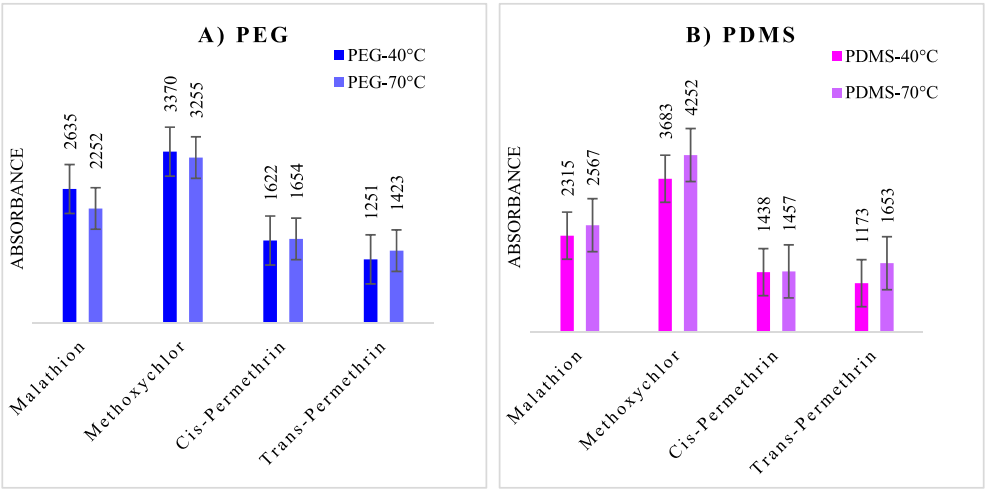

Fig. 7. Graphic representation of the results obtained for the influence of ultrasonic bath temperature: a) PEG-FPSE, b) PDMS-FPSE.

min, and their desorption in ethyl acetate is 120 min.

In the case of PDMS-FPSE, from the graphic representation of the results presented in Fig. 11, it can be observed that the variant that leads to higher values of the areas of the analytes of interest is the one in which the extraction of pesticides by FPSE is 120 min, and their desorption in ethyl acetate is 120 min.

3.2.4. Extraction from textile samples

For a simplified exposure of the results and considering the two types of extraction from the textile fabric, the samples that are exposed directly to the FPSE are noted as" dry", while the samples that are first treated with 500 μL of distilled water are noted as "wet" (see Tables 5 and 6).

The obtained results show slightly increased values in the case of textile materials treated supplementally with distilled water compared to those treated by direct contact. Additionally, the values obtained for the recovery parameter vary as follows:

- ➢ in the case of PEG-FPSE, it varies from 59.3 % (WO-dry for the malathion compound) to 128.0 % (CO/PES-wet for the *trans*-permethrin compound).
- ➢ in the case of PDMS-FPSE, it varies from 52.7 % (CO/PA-wet for the *cis*-permethrin compound) to 123.3 % (CO-wet for the *cis*-permethrin compound).

The percent recovery values of other pesticides evaluated in literature studies and the types of samples analyzed include:

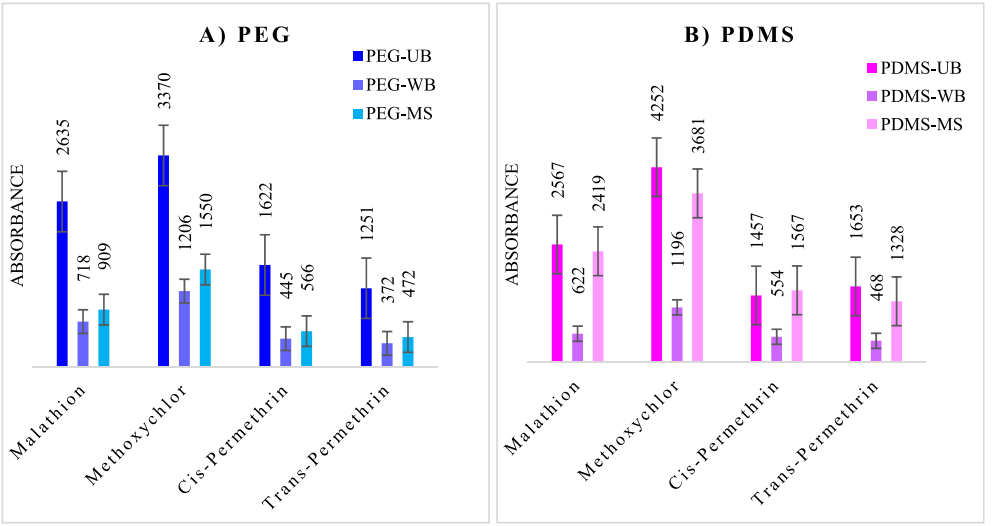

Fig. 8. Graphic representation of the results obtained for the influence of the type of bath: a) PEG-FPSE, b) PDMS-FPSE.

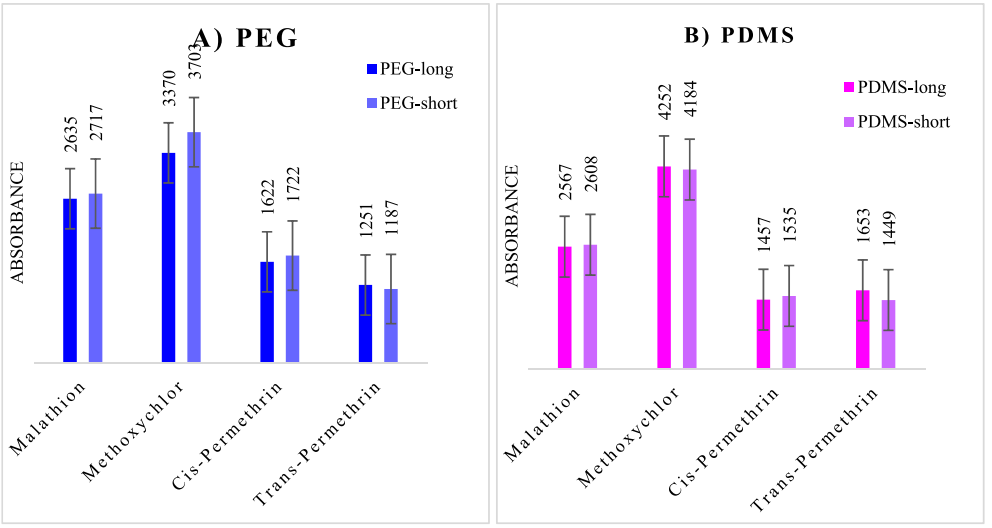

Fig. 9. Graphic representation of the results obtained for the presence or absence of the last preparation steps: a) PEG-FPSE, b) PDMS-FPSE.

- vegetable samples [25], with recovery percentages between 92.4% and 98.5 % for tomatoes, 88.6%–97.9 % for cabbage, 88.9%–95.6 % for eggplant and 91-8%–93.3 % for beans;
- samples of water and fortified fruit juices [27], with recovery percentages between 91.6 % and 99.8 %;
- water samples (river and drinking) [28], with recovery percentages between 22.0 % and 70.0 %.

The results obtained are in line with those presented in the scientific literature, suggesting the appropriateness of the proposed system. Further studies will be carried out for the application of this system on real sample analysis.

4. Conclusions

The paper is significant, as it focuses on assessing the risks to human health posed by the formerly widespread practice of pesticide use by developing and optimizing an innovative non-destructive extraction method, which can be used to assess pesticides from museum textile objects. Both the preparation method of the extraction membrane and the actual extraction method of the analytes of interest from solutions and laboratory textile samples were optimized.

Thus, the system consists of a 100 % cotton fabric coated with a sol-gel solution prepared from a polymer (PEG or PDMS), trimethoxymethylsilane (MTMS), solvent: methylene chloride: acetone (50/50: V/V) and 1 mL trifluoroacetic acid 5 % water.

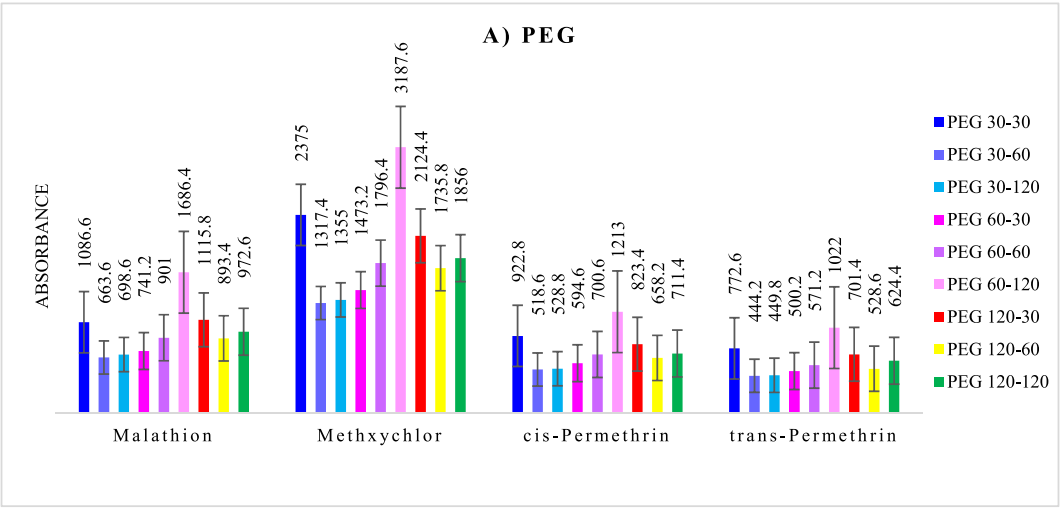

Fig. 10. Graphic representation of the results obtained for the extraction time on PEG-FPSE and desorption time from PEG-FPSE in ethyl acetate.

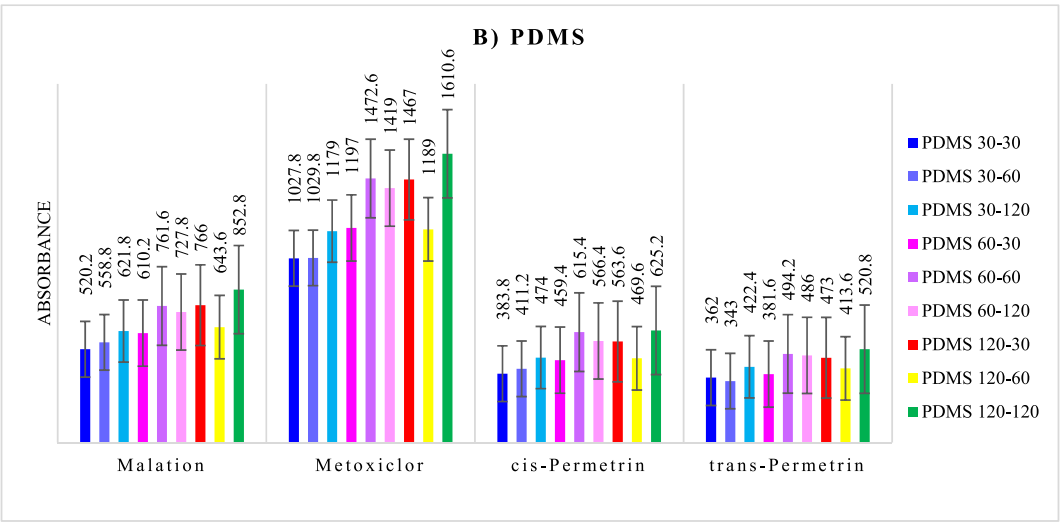

Fig. 11. Graphic representation of the results obtained for the extraction time on PDMS-FPSE and desorption time from PDMS-FPSE in ethyl acetate.

Table 5
Results obtained for the extraction from textile materials with PEG-FPSE.

Sample	Malathion		Methoxychlor		*Cis*-Permethrin		*Trans*-Permethrin	
	ppm	R%	ppm	R%	ppm	R%	ppm	R%
WO-dry	0.9	59.3	1.0	67.3	1.5	101.3	1.5	102.0
WO-wet	1.0	64.67	1.2	76.7	1.5	100.0	1.6	108.7
CO-dry	1.0	64.0	1.1	72.0	1.5	98.0	1.5	101.3
CO-wet	1.1	71.3	1.2	82.0	1.7	112.7	1.7	111.33
CO/PES-dry	1.2	77.3	1.3	86.7	1.1	75.3	1.3	83.3
CO/PES-wet	1.0	67.3	1.2	82.7	1.8	119.3	1.9	128.0
CO/PA-dry	0.9	62.0	0.7	47.3	0.8	52.7	0.8	50.0
CO/PA-wet	0.9	61.3	1.1	70.0	1.6	104.0	1.6	109.3

The extraction method includes the contact of the optimized system with the solution or sample of interest, followed by extraction in ethyl acetate and chromatographic analysis of the resulting solution.

The extraction yields obtained on laboratory textile materials are in the range of 52.667 %–128.000 %.

Table 6
Results obtained for the extraction from textile materials with PDMS-FPSE.

Sample	Malathion		Methoxychlor		*Cis*-Permethrin		*Trans*-Permethrin	
	ppm	R%	ppm	R%	ppm	R%	ppm	R%
WO-dry	0.9	59.3	0.8	52.7	0.9	61.3	1.0	64.0
WO-wet	1.0	67.3	0.9	58.7	1.2	77.3	1.2	80.0
CO-dry	1.6	109.3	1.4	94.7	1.8	121.3	1.8	121.3
CO-wet	1.7	111.3	1.4	92.7	1.9	123.3	1.8	121.3
CO/PES-dry	1.3	86.0	1.1	70.0	1.3	83.3	1.3	86.7
CO/PES-wet	1.6	107.3	1.4	90.0	1.7	116.0	1.8	116.7
CO/PA-dry	1.2	80.0	1.0	66.7	1.2	80.0	1.2	80.7
CO/PA-wet	1.2	80.7	1.0	67.3	1.2	80.7	1.2	80.0

Ethical statement

Not applicable.

Data availability statement

No data was used for the research described in the article.

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CRediT authorship contribution statement

Elena-Cornelia Tanasescu: Writing – review & editing, Writing – original draft, Project administration, Investigation, Conceptualization. **Alexandra-Gabriela Ene:** Writing – original draft, Resources. **Elena Perdum:** Writing – original draft. **Ovidiu Iordache:** Writing – original draft. **Lucia-Oana Secareanu:** Writing – original draft.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:Elena Cornelia Tanasescu reports financial support was provided by Romanian Government Ministry of Research Innovation and Digitization. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] E.C. Tanasescu, M.C. Lite, Harmful health effects of pesticides used on museum textile artifacts – overview, Ecotoxicol. Environ. Saf. 247 (2022) 11420, https://doi.org/10.1016/j.ecoenv.2022.114240.
[2] A. Adriaens, European actions to promote and coordinate the use of analytical techniques for cultural heritage studies, TrAC, Trends Anal. Chem. 23 (8) (2004) 583–586, https://doi.org/10.1016/j.trac.2004.07.001.
[3] A. Adriaens, G. Demortier, COST Actions G1 and G8: EU programs on the use of radiation in art and archaeometry, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 226 (1–2) (2004) 3–9, https://doi.org/10.1016/j.nimb.2004.05.018.
[4] E. Perdum, I.M. Sandulache, D. Toma, D.G. Ciutaru, M. Vamesu, L.O. Secareanu, E.C. Mitran, O.G. Iordache, An analytical approach for extraction and detection of permethrin from functionalized textile materials, Ind. Textil. 70 (2) (2019) 165–169, https://doi.org/10.35530/IT.070.02.1600.
[5] M.T. Domenech-Carbo, Novel analytical methods for characterizing binding media and protective coatings in artworks, Anal. Chim. Acta 621 (2) (2008) 109–139, https://doi.org/10.1016/j.aca.2008.05.056.
[6] Nasa J. La, M. Zanaboni, D. Uldanck, I. Degano, F. Modugno, H. Kutzke, E.S. Tveit, B. Topalova-Casadiego, M.P. Colombini, Novel application of liquid chromatography/mass spectrometry for the characterization of drying oils in art: elucidation on the composition of original paint materials used by Edvard Munch (1863–1944), Anal. Chim. Acta 896 (2015) 177–189, https://doi.org/10.1016/j.aca.2015.09.023.
[7] F.C. Izzo, B. Ferriani, K.J. Van den Berg, H. Van Keulen, E. Zendri, 20th century artists' oil paints: the case of the Olii by Lucio Fontana, J. Cult. Herit. 15 (5) (2014) 557–563, https://doi.org/10.1016/j.culher.2013.11.003.
[8] A. Lluveras-Tenorio, A. Andreotti, I. Bonaduce, S. Boularand, M. Cotte, J. Roqué, M.P. Colombini, M. Vendrell-Saz, Mass Spectrometric and Synchrotron Radiation based techniques for the identification and distribution of painting materials in samples from paints of Josep Maria Sert, Chem. Cent. J. 6 (2012) 1–18, https://doi.org/10.1186/1752-153X-6-45.
[9] B.M. Peake, R. Braund, A. Tong, L.A. Tremblay, The Lifecycle of Pharmaceuticals in the Environment, Elsevier, 2015, pp. 77–107.
[10] S. White, The role of costume mounting in preventive conservation, Stud. Conserv. 39 (sup2) (1994) 228–232, https://doi.org/10.1179/sic.1994.39.Supplement-2.228.
[11] S.B. Hawthorne, D.J. Miller, J. Pawliszyn, C.L. Arthur, Solventless determination of caffeine in beverages using solid-phase microextraction with fused-silica fibers, J. Chromatogr. A 603 (1–2) (1992) 185–191, https://doi.org/10.1016/0021-9673(92)85360-6.

[12] J.H. Lee, S.M. Hwang, D.W. Lee, G.S. Heo, Determination of volatile organic compounds (VOCs) using Tedlar bag/solid phase microextraction/gas chromatography/mass spectrometry (SPME/GC/MS) in ambient and workplace air, Bull. Kor. Chem. Soc. 23 (3) (2002) 488–496, https://doi.org/10.5012/bkcs.2002.23.3.488.
[13] F. Musshoff, H. Junker, B. Madea, Simple determination of 22 organophosphorus pesticides in human blood using headspace solid phase microextraction and gas chromatography with mass spectrometric detection, J. Chromatogr. Sci. 40 (1) (2002) 29–39, https://doi.org/10.1093/chromsci/40.1.29.
[14] A. Sanusi, F. Ferrari, M. Millet, M. Montury, Pesticide vapors in confined atmospheres. Determination of dichlorvos by SPME-GC–MS at the μg m− 3 level, J. Environ. Monit. 5 (4) (2003) 574–577, https://doi.org/10.1039/B302608F.
[15] F. Ferrari, A. Sanusi, M. Millet, M. Montury, Multiresidue method using SPME for the determination of various pesticides with different volatility in confined atmospheres, Anal. Bioanal. Chem. 379 (2004) 476–483, https://doi.org/10.1007/s00216-004-2587-0.
[16] M. Sakamoto, T. Tsutsumi, Applicability of headspace solid phase microextraction to the determination of multiclass pesticides in waters, J. Chromatogr. A 1028 (1) (2004) 63–74, https://doi.org/10.1016/j.chroma.2003.11.066.
[17] M. Bashiri-Juybari, A. Mehdinia, A. Jabbari, Y. Yamini, Determination of Amitraz in the honey samples by dispersive liquid–liquid microextraction followed by gas chromatography—flame ionization detection, Am. J. Anal. Chem. 2 (5) (2011) 632, https://doi.org/10.4236/ajac.2011.25072.
[18] E.G. Amvrazi, M.A. Martini, N.G. Tsiropoulos, Headspace single-drop microextraction of common pesticide contaminants in honey–method development and comparison with other extraction methods, Int. J. Environ. Anal. Chem. 92 (4) (2012) 450–465, https://doi.org/10.1080/03067319.2011.585716.
[19] A. Kabir, K.G. Furton, Fabric phase sorptive extraction: a new generation, green sample preparation approach, in: Solid-Phase Extraction, Elsevier, 2020, pp. 355–386, https://doi.org/10.1016/B978-0-12-816906-3.00013-3.
[20] A. Kabir, V. Samanidou, Fabric phase sorptive extraction: a paradigm shift approach in analytical and bioanalytical sample preparation, Molecules 26 (2021) 865, https://doi.org/10.3390/molecules26040865.
[21] A. Kabir, R. Mesa, J. Jurmain, K. Furton, Fabric phase sorptive extraction explained, Separations 4 (2017) 21, https://doi.org/10.3390/separations402002.
[22] R. Kumar, Heena Gaurav, A.K. Malik, A. Kabir, K.G. Furton, Efficient analysis of selected estrogens using fabric phase sorptive extraction and high-performance liquid chromatography-fluorescence detection, J. Chromatogr. A 1359 (2014) 16–25, https://doi.org/10.1016/j.chroma.2014.07.013.
[23] A. Anthemidis, V. Kazantzi, V. Samanidou, A. Kabir, K.G. Furton, An automated flow injection system for metal determination by flame atomic absorption spectrometry involving on-line fabric disk sorptive extraction technique, Talanta 156–157 (2016) 64–70, https://doi.org/10.1016/j.talanta.2016.05.012.
[24] M. Roldán-Pijuán, R. Lucena, S. Cárdenas, M. Valcárcel, A. Kabir, K.G. Furton, Stir fabric phase sorptive extraction for the determination of triazine herbicides in environmental waters by liquid chromatography, J. Chromatogr. A 1376 (2015) 35–45, https://doi.org/10.1016/j.chroma.2014.12.027.
[25] R. Kaur, R. Kaur, S. Rani, A.K. Malik, A. Kabir, K.G. Furton, Application of fabric phase sorptive extraction with gas chromatography and mass spectrometry for the determination of organophosphorus pesticides in selected vegetable samples, J. Separ. Sci. 42 (2019) 862–870, https://doi.org/10.1002/jssc.201800854.
[26] E.C. Mitran, I.M. Sandulache, C.M. Lite, L.G. Radu, Textile museum collections. SIM method validation for the assessment of pesticides, Mater. Plast. 58 (3) (2021) 1–10, https://doi.org/10.37358/Mat.Plast.1964.
[27] R. Kaur, R. Kaur, S. Rani, A. Malik, A. Kabir, K. Furton, V. Samanidou, Rapid monitoring of organochlorine pesticide residues in various fruit juices and water samples using fabric phase sorptive extraction and gas chromatography-mass spectrometry, Molecules 24 (2019) 1013, https://doi.org/10.3390/molecules24061013.
[28] N. Fontanals, F. Borrull, R.M. Marcé, Fabric phase sorptive extraction for environmental samples, Adv. Sample Prep. 5 (2023) 100050, https://doi.org/10.1016/j.sampre.2022.100050.