ANOVA and Tukey's interpretation of the innovative FPSE method applied to museum textiles

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ABSTRACT – REZUMAT

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The need to protect textile museum collections against pests has led to the use of pesticides. Pesticides can persist over time, thus leading to problems such as possible injury to museum staff. To address this problem, attempts have been made to obtain an overview of pesticide detection without destroying collections.
In this paper, a nondestructive method for the extraction and detection of three pesticides was optimised. The selection of the main parameters of the method was carried out using statistical analysis of the obtained data by applying one-way ANOVA and the Tukey test.
FPSE optimisation is performed by evaluating the following parameters: polymer selection (individual or mixture of polymers), acid catalyst (trifluoroacetic acid, acetic acid and hydrochloride acid), amount of polymer (1 g, 2.5 g or 5 g), polymerisation time (30 minutes, 120 minutes and 240 minutes), ultrasonic bath temperature (40°C and 70°C), type of bath used to obtain the sol-gel (ultrasonic bath, water bath with stirring and mechanical stirrer) and influence of the last steps of the preparation of the sol-gel solution. After the extraction system was optimized, statistical analysis was conducted to assess the influence of pesticide extraction time on FPSE and desorption from FPSE in ethyl acetate.

Keywords: *statistical analysis, coating, extraction methods, nondestructive, chromatography, polymer*

Interpretare ANOVA și Tukey pentru o metodă FPSE inovatoare aplicată textilelor din muzee

Necesitatea de a proteja colecțiile muzeale textile împotriva dăunătorilor a dus la utilizarea pesticidelor. Pesticidele pot persista în timp, ducând la apariția unor probleme ce pot pune în pericol sănătatea personalului muzeelor. Pentru a rezolva această problemă, s-au făcut încercări de a obține o imagine de ansamblu asupra prezenței pesticidelor fără distrugerea colecțiilor.
În această lucrare, a fost optimizată o metodă nedistructivă pentru extracția și detecția a trei pesticide. Selectarea parametrilor principali ai metodei a fost efectuată utilizând analiza statistică a datelor obținute prin aplicarea ANOVA unidirecțională și a testului Tukey.
Optimizarea FPSE s-a realizat prin evaluarea următorilor parametri: selecția polimerului (individual sau amestec de polimeri), catalizatorul acid (acid trifluoracetic, acid acetic și acid clorhidric), cantitatea de polimer (1 g, 2,5 g sau 5 g), timpul de polimerizare (30 minute, 120 minute și 240 minute), temperatura băii cu ultrasunete (40°C și 70°C), tipul de baie utilizată pentru obținerea soluției sol-gel (baie cu ultrasunete, baie de apă cu agitare și agitator mecanic) și influența ultimelor etape de preparare a soluției sol-gel. După optimizarea sistemului de extracție, a fost efectuată o analiză statistică pentru a evalua influența timpului de extracție a pesticidelor pe FPSE și a desorbției de pe FPSE în acetat de etil.

Cuvinte-cheie: *analiză statistică, peliculizare, metode de extracție, nedistructiv, cromatografie, polimer*

INTRODUCTION

Textile fibres are an excellent food source for microbes and insects [1–4]. Various types of pesticides have been used in museum collections, leading to the need to develop methods of extraction, separation, and quantification methods with micro- or even nondestructive characteristics.
From a statistical point of view, the present paper evaluates the possibility of developing a new method of quantifying pesticides that may be present in textile museum collections by coupling a new extraction method (fabric phase sorptive extraction, FPSE) [5] with gas chromatography and mass spectrometry (GC/MS) without prejudicing these collections, which show signs of fragility and deterioration over time. Pesticides have many negative effects on humans and the environment, and it is important and still necessary to develop accurate, sensitive, and robust extraction and analysis methods to determine the amount of pesticides and to maintain compliance with applicable laws. In general, sampling techniques most often involve swabbing, wipe-based sampling of the surfaces of samples or removing part of an object [6], which is important because there is no application in the scientific literature of this extraction

method for museum object analysis. FPSE is a new type of microextraction developed by Kabir and Furton [7]. FPSE uses the sol-gel coating technology developed by Chong et al. [8] to create an inherently porous inorganic-organic hybrid absorbent material that is chemically bonded to the matrix of a flexible and permeable substrate, typically a textile. Table 1 shows some of the applications of the FPSE technique.

The statistical analysis [13] of the results obtained for each stage of the optimization process of the developed analytical system was carried out using Excel and one-way ANOVA [14], followed by a post hoc analysis to highlight the different groups as an average. For this, Tukey's HSD (honestly significant difference) [15] test, a test based on the comparison of two-by-two groups at a confidence interval of 95%, was selected for this analysis.

In the case of the one-way ANOVA method, the following two hypotheses were established:

- Null hypothesis – H0: the obtained values are independent, without a significant difference.
- Alternative hypothesis – H1: the obtained values are dependent, with significant differences.

The two proposed hypotheses are verified by determining the Pearson coefficient, "p", at a 95% confidence interval [16], with $p > 0.05$ indicating that the null hypothesis is accepted: from a statistical point of view, the difference is not significant, and $p < 0.05$ indicates that the null hypothesis is rejected; from a statistical point of view, the difference is significant.

To perform the Tukey test, the q_Tukey value was determined by comparing groups pairwise, and then the standardized critical q value was determined based on the number of groups and degrees of freedom.

- If q-Tukey > q-critical, there is a significant difference.
- If q-Tukey < q-critical: there is an insignificant difference.

The calculation formula for the q value is presented as follows:

$$q\text{-Tukey} = \frac{M_i - M_j}{\sqrt{\frac{Ms_{intra}}{n}}} \quad (1)$$

where M_i, M_j – means of the two compared groups, Ms_{intra} is the intragroup mean square and n is the number of measurements in the group.

MATERIALS AND METHODS

The materials and reagents used were 100% cotton fabric, polymer (polyethylene glycol (PEG), dimethylpolysiloxane (PDMS), polylactic acid (PLA) and ethyl cellulose (EC)), and trimethoxymethylsilane (MTMS). The solvent used was methylene chloride: acetone (50/50: V/V), trifluoroacetic acid 5% water (TFA), acetic acid 5% water (AA), and hydrochloric acid 5% water (HCl). For the pesticide solutions, all reagents used were Pestanal® grades: malathion, methoxychlor, and permethrin (consisting of cis and trans isomers) as pesticides of interest and ethyl acetate as the solvent for the pesticide solution.

First, the sol-gel solution was prepared with 2.5 g of polymer, 2.5 ml of MTMS, 5 ml of solvent and 1 ml of 5% TFA. After the sol-gel solution was obtained, the textile support was cut into 5 cm × 5 cm pieces, which were immersed in the solution and allowed to polymerize. Thus, the Polymer-FPSE was obtained.

Fabric phase sorptive extraction of pesticides is achieved by introducing one square of 1 cm × 1 cm Polymer-FPSE into 1 ml of 100 ppm pesticide mix solution and keeping it for 30 minutes at room temperature. Next, the Polymer-FPSE was removed, left for 1 min at room temperature and then placed in 2 ml of ethyl acetate for pesticide extraction. After the extraction time, the solution was injected into the chromatographic system coupled with a mass spectrometer detector.

FPSE optimisation was performed by evaluating parameters such as polymer selection (individual or mixture of polymers), acid catalyst (trifluoroacetic acid, acetic acid and hydrochloride acid), amount of polymer (1 g, 2.5 g or 5 g), polymerisation time (30 minutes, 120 minutes and 240 minutes), ultrasonic bath temperature (40°C and 70°C), and type of bath used to obtain the sol-gel (ultrasonic bath, water bath with stirring and mechanical stirrer).

The last step in the preparation of the sol-gel solution was stirring the reaction vessel for 15 minutes at room temperature at a speed of 450 rpm using a mechanical stirrer, after which the obtained mixture

Table 1

APPLICATION OF THE FPSE TECHNIQUE (ADAPTED FROM ZILFIDOU ET AL.) [9]

System	Support	Polymer	Sample	Reference
FPSE-HPLC-UV	Cellulose	PEG	Tapp water Substituted phenols	[5]
FPSE-HS-GC-MS	Fibreglass	PDMDPS	Ambient air Sex pheromone	[10]
FDSE-FI-FAAS	Polyester	PDMDPS	River water Heavy metals	[11]
SE/GC–MS	Celluloses	CW/PTHF/PDMS	Vegetable Organophosphorus pesticides	[12]

was centrifuged for 5 minutes at a speed of 5000 rpm at 20°C. The influence of the last steps for sol-gel preparation is verified to obtain a shorter preparation method. To optimize FPSE, the influence of pesticide extraction time on FPSE and desorption from FPSE in ethyl acetate was also assessed.
A schematic representation of the process is presented in figure 1.

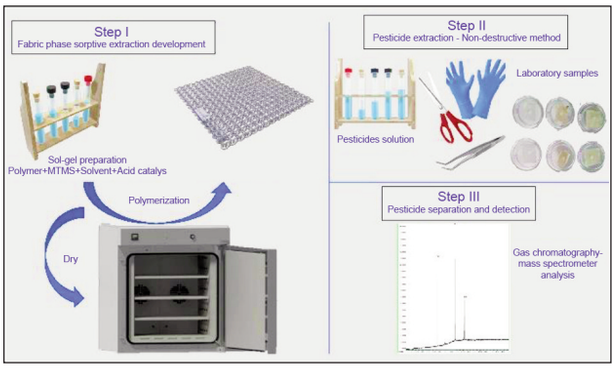

Fig. 1. Fabric phase sorptive extraction development

RESULTS AND DISCUSSION

To facilitate the presentation of the results, in the case of the application of one-way ANOVA, the results will be interpreted in the form of "p<0.05" or "p>0.05". In the case of the Tukey test, if there is a significant difference, the result will be noted with "S", and if there is an insignificant difference, the result will be noted with "I". To complete the statistical analysis, five measurements for each sample were performed.

Polymer selection

The chromatographic peak area values of the polymers used in the study obtained after measurements are given in table 2 and the ANOVA results are given in table 3.
In all cases, $p < 0.05$ indicated a significant difference between groups.

Table 3

ANOVA RESULTS FOR THE INFLUENCE OF POLYMER

Pesticides	P value between groups
Malathion	p<0.05
Methoxychlor	p<0.05
cis-Permethrin	p<0.05
trans-Permethrin	p<0.05

To evaluate which group was different, Tukey's test was performed. Due to the substantial number of pairs (91 pairs) in table 4, only the results obtained for the pairs with PEG and PDMS, the polymers that presented the largest area (25 pairs), are presented.
The obtained results indicate significant differences for all the polymer variants used. Considering these differences, two individual polymers, PEG and PDMS, will be utilized, and the results obtained for these 2 variants will be evaluated. The notation of the extraction method in which PEG is used is PEG-FPSE, and that in which PDMS is used is PDMS-FPSE.

Acid catalyst influence

The chromatographic peak area values of the acid catalysts used in the study obtained after measurements are given in table 5 and the ANOVA results are given in table 6.
Except for trans-permethrin, where the null hypothesis is accepted, meaning that the obtained values are independent, without a significant difference, for the remaining analytes of interest, the null hypothesis is rejected, indicating a significant difference. In the case of PEG-FPSE, the analysis of the sample with hydrochloric acid could not be performed, as the textile support was degraded. Thus, the interpretation will be performed using the results obtained after the application of one-way ANOVA. In this case, the comparison was made for PEG-AA vs. PEG-TFA. Tukey's

Table 2

CHROMATOGRAPHIC PEAK AREA OBTAINED FOR POLYMER SELECTION

Area	PEG	PDMS	PLA	EC	PEG/PDMS	PEG/PLA	PEG/EC
Inj 1	1661	888	1609	1073	839	1277	1661
Inj 2	1666	889	1630	1079	840	1276	1666
Inj 3	1668	880	1618	1097	839	1289	1668
Inj 4	1668	888	1579	1088	836	1252	1668
Inj 5	1665	870	1578	1080	834	1243	1665
Area	**PDMS/PLA**	**PDMS/EC**	**PLA/EC**	**PEG/PDMS/PLA**	**PEG/PDMS/EC**	**PDMS/PLA/EC**	**PEG/PDMS/PLA/EC**
Inj 1	527	1384	1266	798	1213	827	887
Inj 2	523	1409	1273	799	1212	837	898
Inj 3	527	1386	1303	796	1217	854	922
Inj 4	546	1408	1318	806	1231	811	913
Inj 5	539	1380	1288	798	1189	817	892

Note: Inj – injection number.

Table 4

TUKEY TEST RESULTS FOR THE INFLUENCE OF POLYMERS				
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**	**trans-Permethrin**
PEG vs. PDMS	S	S	S	S
PEG vs. PLA	S	S	S	S
PEG vs. EC	S	S	S	S
PEG vs. PEG/PDMS	S	S	S	S
PEG vs. PEG/PLA	S	S	S	S
PEG vs. PEG/EC	S	S	S	S
PEG vs. PDMS/PLA	S	S	S	S
PEG vs. PDMS/EC	S	S	S	S
PEG vs. PLA/EC	S	S	S	S
PEG vs. PEG/PDMS/PLA	S	S	S	S
PEG vs. PEG/PDMS/EC	S	S	S	S
PEG vs. PDMS/PLA/EC	S	S	S	S
PEG vs. PEG/PDM/PLA/EC	S	S	S	S
PDMS vs. PLA	S	S	S	S
PDMS vs. EC	S	S	S	S
PDMS vs. PEG/PDMS	S	S	S	S
PDMS vs. PEG/PLA	S	S	S	S
PDMS vs. PEG/EC	S	S	S	S
PDMS vs. PDMS/PLA	S	S	S	S
PDMS vs. PDMS/EC	S	S	S	S
PDMS vs. PLA/EC	S	S	S	S
PDMS vs. PEG/PDMS/PLA	S	S	S	S
PDMS vs. PEG/PDMS/EC	S	S	S	S
PDMS vs. PDMS/PLA/EC	S	S	S	S
PDMS vs. PEG/PDM/PLA/EC	S	S	S	S

Table 5

CHROMATOGRAPHIC PEAK AREA OBTAINED FOR THE ACID CATALYST INFLUENCE						
Area	**PEG-1 g**	**PEG-2.5 g**	**PEG-5 g**	**PDMS-1 g**	**PDMS-2.5 g**	**PDMS-5 g**
Inj 1	691	1499	916	625	1661	556
Inj 2	652	1498	935	618	1666	539
Inj 3	692	1494	898	601	1668	557
Inj 4	651	1495	935	639	1668	571
Inj 5	670	1488	926	637	1665	547

Note: Inj – injection number.

Table 6

ANOVA RESULTS FOR THE ACID CATALYST INFLUENCE					
Area	**PEG-AA**	**PEG-TFA**	**PDMS-AA**	**PDMS-HCl**	**PDMS-TFA**
Inj 1	1009	1499	1171	913	1661
Inj 2	1019	1498	1172	911	1666
Inj 3	1039	1494	1182	941	1668
Inj 4	1033	1495	1171	908	1668
Inj 5	1047	1488	1183	933	1665

Note: Inj – injection number.

test was applied to the PDMS-FPSE samples for all analytes of interest.

As shown in table 7 and table 8, the only insignificant difference appears in the case of trans-permethrin: for both PDMS-FPSE and PEG-FPSE, both TFA and AA were present. For the remaining compounds, the differences are significant, and the type of acid used influences the results. Taking into account these results, ***trifluoracetic acid*** was further used.

Table 7

TUKEY TEST RESULTS FOR THE ACID CATALYST INFLUENCE		
Pesticides	**P value between groups**	
	PEG – FPSE	**PDMS – FPSE**
Malathion	p<0.05	p<0.05
Methoxychlor	p<0.05	p<0.05
cis-Permethrin	p<0.05	p<0.05
trans-Permethrin	p>0.05	p<0.05

Table 8

TUKEY TEST RESULTS FOR PDMS-FPSE				
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**	**trans-Permethrin**
PDMS-AA vs. PDMS-HCl	S	S	S	S
PDMS-AA vs. PDMS-TFA	S	S	S	I
PDMS-HCl vs. PDMS-TFA	S	S	S	S

Polymer quantity influence

The chromatographic peak area values of the polymer quantity used in the study obtained after measurements are given in table 9 and the ANOVA results are given in table 10.

In all cases, $p < 0.05$ resulting in a significant difference between groups (table 11).

Table 9

CHROMATOGRAPHIC PEAK AREA OBTAINED FOR THE POLYMER QUANTITY INFLUENCE						
Area	**PEG-1 g**	**PEG-2.5 g**	**PEG-5 g**	**PDMS-1 g**	**PDMS-2.5 g**	**PDMS-5 g**
Inj 1	691	1499	916	625	1661	556
Inj 2	652	1498	935	618	1666	539
Inj 3	692	1494	898	601	1668	557
Inj 4	651	1495	935	639	1668	571
Inj 5	670	1488	926	637	1665	547

Note: Inj – injection number.

Table 10

ANOVA RESULTS FOR THE POLYMER QUANTITY INFLUENCE		
Pesticides	**P value between groups**	
	PEG – FPSE	**PDMS – FPSE**
Malathion	p<0.05	p<0.05
Methoxychlor	p<0.05	p<0.05
cis-Permethrin	p<0.05	p<0.05
trans-Permethrin	p<0.05	p<0.05

Table 11

TUKEY TEST RESULTS FOR THE POLYMER QUANTITY INFLUENCE				
PEG-FPSE				
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**	**trans-Permethrin**
PEG-1g vs PEG-2.5g	S	S	S	S
PEG-1g vs PEG-5g	S	S	S	S
PEG-2.5g vs PEG-5g	S	S	S	S
PDMS-FPSE				
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**	**trans-Permethrin**
PDMS-1g vs. PDMS-2.5g	S	S	S	S
PDMS-1g vs. PDMS-5g	S	S	S	I
PDMS-2.5g vs. PDMS-5g	S	S	S	S

Except for PDMS-1g vs PDMS-5g for trans-permethrin, where the difference is insignificant, for the rest of the compounds, the amount of polymer used significantly influences the results, so the version with ***2.5 g polymer*** will be used for the following steps.

Influence of polymerisation time

The chromatographic peak area values of the polymerization time used in the study obtained after measurements are given in table 12 and the ANOVA results are given in table 13.

In all cases, $p < 0.05$ indicated a significant difference between groups (table 14).

The only insignificant difference occurs in the case of PEG-120 minutes vs. PEG-240 minutes for methoxychlor because either of the two variants can be used for this compound. For the other compounds, the polymerization time led to significantly different results. For the subsequent experiments, the polymerization time was ***30 minutes***.

Bath temperature influence

The chromatographic peak area values of the bath temperature used in the study obtained after measurements are given in table 15 and the ANOVA results are given in table 16.

Given that the one-way ANOVA-test is initially applied for the evaluation of two groups (40°C and 70°C), it is no longer necessary to perform the Tukey test, and the statistical evaluation can be carried out based on the coefficient *p*.

Thus, in the case of cis-permethrin, the null hypothesis, H0, is accepted for both PEG-FPSE and PDMS-FPSE, and the obtained values are independent, without a significant difference. For the remaining compounds, the alternative hypothesis, H1, is accepted, and the obtained values are dependent, which shows significant differences. Next, for the PEG-FPSE and PDMS-FPSE variants, a ***temperature of 70ºC*** was used.

Table 12

CHROMATOGRAPHIC PEAK AREA OBTAINED FOR THE POLYMERIZATION TIME INFLUENCE

Area	PEG - 30 minutes	PEG - 120 minutes	PEG - 240 minutes	PDMS - 30 minutes	PDMS - 120 minutes	PDMS - 240 minutes
Inj 1	2269	1499	1688	2578	1661	2136
Inj 2	2253	1498	1671	2582	1666	2135
Inj 3	2259	1494	1670	2561	1668	2136
Inj 4	2231	1495	1671	2572	1668	2122
Inj 5	2248	1488	1668	2544	1665	2116

Note: Inj – injection number.

Table 13

ANOVA RESULTS FOR THE POLYMERIZATION TIME INFLUENCE

Pesticides	P value between groups	
	PEG – FPSE	PDMS – FPSE
Malathion	p<0.05	p<0.05
Methoxychlor	p<0.05	p<0.05
cis-Permethrin	p<0.05	p<0.05
trans-Permethrin	p<0.05	p<0.05

Table 14

TUKEY TEST RESULTS FOR THE POLYMERIZATION TIME INFLUENCE

TUKEY TEST RESULTS FOR PEG-FPSE				
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**	**trans-Permethrin**
PEG-30 minutes vs. PEG-120 minutes	S	S	S	S
PEG-30 minutes vs. PEG-240 minutes	S	S	S	S
PEG-120 minutes vs. PEG-240 minutes	S	I	S	S
TUKEY TEST RESULTS FOR PDMS-FPSE				
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**	**trans-Permethrin**
PDMS-30 minutes vs. PDMS-120 minutes	S	S	S	S
PDMS-30 minutes vs. PDMS-240 minutes	S	S	S	S
PDMS-120 minutes vs. PDMS-240 minutes	S	S	S	S

Table 15

CHROMATOGRAPHIC PEAK AREA OBTAINED FOR THE BATH TEMPERATURE INFLUENCE				
Area	**PEG-40°C**	**PEG-70°C**	**PDMS-40°C**	**PDMS-70°C**
Inj 1	2643	2269	2352	2578
Inj 2	2595	2253	2310	2582
Inj 3	2660	2259	2296	2561
Inj 4	2645	2231	2261	2572
Inj 5	2633	2248	2356	2544

Note: Inj – injection number.

Table 16

ANOVA RESULTS FOR THE BATH TEMPERATURE INFLUENCE		
Pesticides	**P value between groups**	
	PEG – FPSE	**PDMS – FPSE**
Malathion	p<0.05	p<0.05
Methoxychlor	p<0.05	p<0.05
cis-Permethrin	p>0.05	p>0.05
trans-Permethrin	p<0.05	p<0.05

Bath type influence

The chromatographic peak area values of the bath type used in the study obtained after measurements are given in table 17 and the ANOVA results are given in table 18.

In all cases, $p < 0.05$ indicated a significant difference between groups (table 19).

The type of bath used to make the sol-gel solution led to significant differences for all compounds, regardless of the type of polymers used (PEG or PDMS), except the compound cis-Permethrin. For this compound, there is an insignificant difference between PDMS-UB and PDMS-MS. Thus, for this analyte, either of the two options can be utilized. Considering the obtained results, an ***ultrasound bath*** was utilized.

The final steps of sol-gel preparation influence

The chromatographic peak area values of the last steps for sol-gel preparation used in the study obtained after measurements are given in table 20 and the ANOVA results are given in table 21.

In this case, the statistical analysis of the results will be carried out via one-way ANOVA:

– the null hypothesis, H0 (the obtained values are independent, without a significant difference), is accepted in the case of PEG-FPSE for trans-permethrin and in the case of PDMS-FPSE for malathion and cis-Permethrin.
– the alternative hypothesis, H1 (the obtained values are dependent, with significant differences) is accepted in the case of PEG-FPSE for malathion, methoxy-

Table 17

CHROMATOGRAPHIC PEAK AREA OBTAINED FOR THE BATH TYPE INFLUENCE						
Area	**PEG-UB**	**PEG-WB**	**PEG-MS**	**PDMS-UB**	**PDMS-WB**	**PDMS-MS**
Inj 1	2643	718	911	2578	622	2372
Inj 2	2595	738	909	2582	619	2488
Inj 3	2660	719	902	2561	610	2448
Inj 4	2645	708	917	2572	614	2404
Inj 5	2633	708	908	2544	643	2384

Note: Inj – injection number.

Table 18

ANOVA RESULTS FOR THE BATH TYPE INFLUENCE		
Pesticides	**P value between groups**	
	PEG – FPSE	**PDMS – FPSE**
Malathion	p<0.05	p<0.05
Methoxychlor	p<0.05	p<0.05
cis-Permethrin	p<0.05	p<0.05
trans-Permethrin	p<0.05	p<0.05

Table 19

TUKEY TEST RESULTS FOR THE BATH TYPE INFLUENCE				
TUKEY TEST RESULTS FOR PEG-FPSE				
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**	**trans-Permethrin**
PEG-UB vs. PEG-WB	S	S	S	S
PEG-UB vs. PEG-MS	S	S	S	S
PEG-WB vs. PEG-MS	S	S	S	S
TUKEY TEST RESULTS FOR PDMS-FPSE				
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**	**trans-Permethrin**
PDMS-UB vs. PDMS-WB	S	S	S	S
PDMS-UB vs. PDMS-MS	S	S	I	S
PDMS-WB vs. PDMS-MS	S	S	S	S

Table 20

CHROMATOGRAPHIC PEAK AREA OBTAINED FOR THE SOL-GEL PREPARATION LAST STEPS INFLUENCE				
Area	**PEG-long**	**PEG-short**	**PDMS-long**	**PDMS-short**
Inj 1	2643	2684	2578	2516
Inj 2	2595	2757	2582	2666
Inj 3	2660	2732	2561	2589
Inj 4	2645	2708	2572	2550
Inj 5	2633	2705	2544	2718

Note: Inj – injection number.

Table 21

ANOVA RESULTS FOR THE SOL-GEL PREPARATION LAST STEPS INFLUENCE		
Pesticides	**P value between groups**	
	PEG – FPSE	**PDMS – FPSE**
Malathion	p<0.05	p>0.05
Methoxychlor	p<0.05	p<0.05
cis-Permethrin	p<0.05	p>0.05
trans-Permethrin	p>0.05	p<0.05

chlor and cis-permethrin, and in the case of PDMS-FPSE for methoxychlor and trans-permethrin. Considering these results, a ***short version*** of the method will be used, eliminating the last operations from the preparation of the sol-gel solution.

Influence of pesticide extraction time

The chromatographic peak area values of the extraction-desorption time used in the study obtained after measurements are given in table 22 and the ANOVA results are given in table 23.

Table 22

CHROMATOGRAPHIC PEAK AREA OBTAINED FOR EXTRACTION-DESORPTION TIME OF PESTICIDE INFLUENCE									
Area	**PEG 30-30**	**PEG 30-60**	**PEG 30-120**	**PEG 60-30**	**PEG 60-60**	**PEG 60-120**	**PEG 120-30**	**PEG 120-60**	**PEG 120-120**
Inj 1	1074	658	693	724	898	1697	1107	883	950
Inj 2	1072	678	701	753	910	1677	1132	912	990
Inj 3	1100	672	707	759	905	1687	1126	899	982
Inj 4	1092	667	693	739	898	1690	1112	890	975
Inj 5	1095	643	699	731	894	1681	1102	883	966
Area	**PDMS 30-30**	**PDMS 30-60**	**PDMS 30-120**	**PDMS 60-30**	**PDMS 60-60**	**PDMS 60-120**	**PDMS 120-30**	**PDMS 120-60**	**PDMS 120-120**
Inj 1	507	562	616	600	756	717	744	621	831
Inj 2	530	568	638	621	769	752	795	671	891
Inj 3	522	568	628	619	766	734	774	654	859
Inj 4	512	544	609	606	761	723	764	643	841
Inj 5	530	552	618	605	756	713	753	629	842

Note: Inj – injection number.

Table 23

ANOVA RESULTS FOR THE EXTRACTION-DESORPTION TIME OF PESTICIDE INFLUENCE		
Pesticides	**P value between groups**	
	PEG – FPSE	**PDMS – FPSE**
Malathion	p<0.05	p<0.05
Methoxychlor	p<0.05	p<0.05
cis-Permethrin	p<0.05	p<0.05
trans-Permethrin	p>0.05	p<0.05

Except for PEG-FPSE, for trans-permethrin, $p < 0.05$ resulted in a significant difference between groups.
To facilitate the varying extraction times, the pairwise structure will be of the *x–y* type, where "x" represents the pesticide extraction time on the extraction system (PEG-FPSE or PDMS-FPSE) and "y" represents the pesticide extraction time on the system of extraction into the extraction solvent (ethyl acetate).
For example, 30–30 means that the FPSE is placed for 30 minutes on the lab sample and for another 30 minutes in the extraction solvent (table 24).

Table 24

TUKEY TEST RESULTS FOR PEG-FPSE			
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**
30-30 vs. 30-60	S	S	S
30-30 vs. 30-120	S	S	S
30-30 vs. 60-30	S	S	S
30-30 vs. 60-60	S	S	S
30-30 vs. 60-120	S	S	S
30-30 vs. 120-30	S	S	S
30-30 vs. 120-60	S	S	S
30-30 vs. 120-120	S	S	S
30-60 vs. 30-120	S	I	I
30-60 vs. 60-30	S	S	S
30-60 vs. 60-60	S	S	S
30-60 vs. 60-120	S	S	S
30-60 vs. 120-30	S	S	S
30-60 vs. 120-60	S	S	S
30-60 vs. 120-120	S	S	S
30-120 vs. 60-30	S	S	S
30-120 vs. 60-60	S	S	S
30-120 vs. 60-120	S	S	S
30-120 vs. 120-30	S	S	S
30-120 vs. 120-60	S	S	S
30-120 vs. 120-120	S	S	S
60-30 vs. 60-60	S	S	S
60-30 vs. 60-120	S	S	S
60-30 vs. 120-30	S	S	S
60-30 vs. 120-60	S	S	S
60-30 vs. 120-120	S	S	S
60-60 vs. 60-120	S	S	S
60-60 vs. 120-30	S	S	S
60-60 vs. 120-60	I	I	I
60-60 vs. 120-120	S	I	I
60-120 vs. 120-30	S	S	S
60-120 vs. 120-60	S	S	S
60-120 vs. 120-120	S	S	S
120-30 vs. 120-60	S	S	S
120-30 vs. 120-120	S	S	S
120-60 vs. 120-120	S	S	S

Table 25

TUKEY TEST RESULTS FOR PDMS-FPSE				
Pair	**Malathion**	**Methoxychlor**	**cis-Permethrin**	**trans-Permethrin**
30-30 vs. 30-60	S	S	S	I
30-30 vs. 30-120	S	S	S	S
30-30 vs. 60-30	S	S	S	S
30-30 vs. 60-60	S	S	S	S
30-30 vs. 60-120	S	S	S	S
30-30 vs. 120-30	S	I	S	I
30-30 vs. 120-60	S	S	S	S
30-30 vs. 120-120	S	S	I	I
30-60 vs. 30-120	S	S	S	I
30-60 vs. 60-30	S	S	S	S
30-60 vs. 60-60	S	S	S	S
30-60 vs. 60-120	S	S	S	S
30-60 vs. 120-30	S	S	I	I
30-60 vs. 120-60	S	S	S	S
30-60 vs. 120-120	S	S	S	I
30-120 vs. 60-30	I	S	S	I
30-120 vs. 60-60	S	S	S	S
30-120 vs. 60-120	S	I	I	I
30-120 vs. 120-30	S	S	S	I
30-120 vs. 120-60	I	I	I	I
30-120 vs. 120-120	S	S	S	S
60-30 vs. 60-60	S	I	I	I
60-30 vs. 60-120	S	S	S	I
60-30 vs. 120-30	S	S	S	S
60-30 vs. 120-60	S	S	S	I
60-30 vs. 120-120	S	S	S	S
60-60 vs. 60-120	S	S	S	I
60-60 vs. 120-30	I	S	S	S
60-60 vs. 120-60	S	S	S	S
60-60 vs. 120-120	S	S	S	S
60-120 vs. 120-30	S	S	S	S
60-120 vs. 120-60	S	I	I	I
60-120 vs. 120-120	S	S	S	S
120-30 vs. 120-60	S	S	S	I
120-30 vs. 120-120	S	S	S	I
120-60 vs. 120-120	S	S	S	S

As shown in table 25, most of the obtained results indicate significant differences, with *q*-Tukey > *q*-critic. For PEG-FPSE, the pesticide extraction time on FPSE was 60 minutes, and the pesticide desorption time from FPSE in ethyl acetate was 120 minutes.
For PDMS-FPSE, the pesticide extraction time on FPSE was 120 minutes, and the pesticide desorption time from FPSE in ethyl acetate was 120 minutes.

CONCLUSIONS

In the present work, an innovative analytical system was developed and optimized based on nondestructive extraction and chromatographic analysis of the obtained samples. Fabric phase sorptive extraction was proposed for the determination of 3 pesticides (malathion, methoxychlor and permethrin: cis- and trans-isomers) that may be present in modern and contemporary textile objects. The evaluated parameters are listed as follows: polymer selection (individual or mixture of polymers), acid catalyst (trifluoroacetic acid, acetic acid and hydrochloride acid), amount of polymer (1 g, 2.5 g or 5 g), polymerisation time (30 minutes, 120 minutes and 240 minutes), ultrasonic bath temperature (40°C and 70°C), type of bath used to obtain the sol-gel (ultrasonic bath, water bath with stirring and mechanical stirrer) and the influence of the final steps of the preparation of the sol-gel solution. Moreover, the influence of pesticide extraction time on FPSE and desorption from FPSE in ethyl acetate was assessed.
The first step consisted of using one-way ANOVA, for which two hypotheses were issued: the null hypothesis (the obtained values are independent, without a significant difference) and the alternative hypothesis

(the obtained values are dependent, with a significant difference). The two hypotheses were tested for a 95% confidence interval. When the alternative hypothesis was accepted and more than two groups of data were compared, Tukey's test was used to investigate which group showed different data, and depending on this result, the working parameter was selected.

By applying two statistical methods, the working parameters of the extraction system and the extraction of 3 pesticides of interest, namely, malathion, methoxychlor and permethrin (two cis- and trans-isomers), were selected.

This study provides new approaches for expanding scientific knowledge in the field of determining pesticides present in modern and contemporary textile objects and substantiates the performance of a new nondestructive method of extraction, separation, and detection of these compounds.

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