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DOCTORAL THESIS SUMMARY

Integrated analytical systems for the evaluation of modern and contemporary textile museum collections

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Keywords: *analytical systems, pesticides, fabric phase sorptive extraction, museum collections*

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**The table of contents respects the page numbering of the doctoral thesis. At the same time, the numbers of the figures, tables, equations, and bibliographic sources in this summary correspond to those in the doctoral thesis.*

THANKS

No other animals have ever lighted fires as far as we can tell. In field archaeology, a charcoal deposit found in such a location that it could not have been made by a forest fire is taken as conclusive evidence of man. A circular dark disk in the soil five or six feet in diameter is such a find ... With ... modern radioactive dating methods, we can trace man's history.

— Willard Frank Libby [1]

I would like to thank the PhD supervisor, Prof. PhD Eng. Gabriel-Lucian Radu, for his support and patience during the development of this doctoral thesis. Under your guidance I went through all the difficulties, overcame them, and got an excellent start for further achievements.
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I would especially like to thank my husband, Alexandru, who believed in me and what I could achieve. Thank you for being my support and for motivating and encouraging me to keep going, even when I want to give up.
I also thank my family and especially my parents for their constant support and love and education without which I would not have become the person I am today both personally and professionally.
In closing, I would like to thank everyone who has guided me or given me support to complete this stage in my life.

INTRODUCTION

The subject of the doctoral thesis "**Integrated analytical systems for the evaluation of modern and contemporary textile museum collections**" brings to the fore the importance of monitoring textile collections from the point of view of identifying toxic compounds that can harm human health, but also the environment.

The subject proposed and presented in the paper evaluates the possibility of developing a new analysis method for the identification and monitoring of pesticides, without prejudicing these collections, which show signs of fragility and deterioration over time.

Ethnographic textile pieces are complex, both in terms of the component materials and in terms of the techniques used to manufacture them. The act of preserving the cultural and artistic heritage is first a matter of scientific research and then of technical execution.

There is no doubt about the importance of textiles as a reflection of both present and past cultures. Museum materials provide a wealth of information about ancient cultures, the techniques and technologies of textile fabrics, and the relationship of these objects to their ceremonial and everyday use.

Textile objects contaminated with various toxic substances (e.g. pesticides) are not a completely new problem for museum workers and beyond. All collections of a museum or collectors are made of organic materials (such as textiles, leather, feathers, wood, plant materials, etc.) and will be more than likely contaminated.

Currently, although the danger posed by the possible existence of pesticides is known to museum staff and those who deal with art objects and textile collections, there may be isolated cases, in small museums or historic houses, where staff may not to be aware of the possibility of being exposed to risks that may endanger their health.

An example is silk textiles, which may contain arsenic and lead added during the manufacturing process and present a serious health hazard[2]. Lead quickly oxidizes into a fine white powder that can easily be inhaled, ingested or contained in clothing[2]. Moreover, many substances once considered safe in the past may turn out to be dangerous today, such as asbestos[3].

There are also those collectibles treated in the past with various pesticides, but which have not been highlighted in any document[3], thus endangering the health of museum staff and collectors. Objects treated with pesticides at the time of purchase or collection of such already treated objects that were later transferred to museums were often re-treated with chemicals by museum staff as a method of preventing pest infestation. These objects treated with various chemicals can endanger people's health, but the actions of the staff in the past should not be

criticized. There are clear records of the fact that certain collections made of organic material would not have lasted over time without these treatments[4].

What can be done next is to create a way to protect the personnel handling the collections and more than that: an assessment of the presence of pesticides and their possible removal.

Advanced analytical methods and techniques represent an essential option in the field of our cultural heritage, as they provide the means to investigate the researched objects[5,6]. In the case of the analysis of ancient, modern and contemporary materials, it is very important to keep the artifacts intact, as they cannot be replaced, and the consumption or damage of even a small part of them for analytical purposes should only be undertaken if the data do not can be obtained otherwise.

There is a list made by Lahanier and his collaborators[7] in which he show the ideal characteristics that an analytical method should present in order to be applied in the analysis of heritage objects:

- to be non-destructive;
- to be fast;
- to be universal – so that materials and objects of different sizes and shapes can be analysed with minimal pre-treatment of the sample;
- to be versatile – as to allow obtaining average compositional information, as well as local information of small areas (e.g. millimetre to micron) from heterogeneous materials;
- to be sensitive;
- to be multi-elemental.

THE OBJECTIVES OF THE DOCTORAL THESIS

The selection of the analytical method that leads to the best resolution of the pursued goal[8] is the first step in a fundamental scientific approach.

Within the work, the development of an integrated analytical system for the evaluation of modern and contemporary textile museum collections was considered for the evaluation of three types of pesticides that may be present in modern and contemporary textile objects: malathion, methoxychlor and permethrin.

The determination of organic pesticides can be problematic due to their volatility, so the choice of the analysis method must be made with this aspect in mind. Gas chromatography is one of the most used analytical techniques for the separation of volatile organic components that can

be present in modern and contemporary art objects[9,10]. Mass spectrometry (MS) is a widely used technique for pesticide detection due to its very good sensitivity and ability to provide structural information about the analysed compounds. However, MS as a stand-alone technique cannot be used for the quantitative and qualitative analysis of complex mixtures, due to numerous limitations (eg: matrix effects, difficulty in assigning signals from the mass spectrum if the sample is a mixture). These shortcomings can be reduced or eliminated by coupling mass spectrometry with gas chromatography.

The main original scientific and technical contributions obtained following the approach to the subject consisted in:

- *the development of new sample preparation* methods based on fabric phase sorptive extraction of pesticides present in modern and contemporary textile objects that ensure reproducibility and recovery yields comparable to the results of extraction techniques used so far;
- *optimization of extraction parameters (*polymers, time and temperature) depending on the textile material type;
- *the development of a selective and fast chromatographic method* that allows the quantification with a high degree of reproducibility of the pesticides present in modern and contemporary textile objects;
- *optimizing the working parameters* of the chromatographic method used in the separation so that the highest possible selectivity and high reproducibility can be obtained for complex mixtures of the analytes of interest;
- *validation of a high-performance method* of pesticide identification and quantification that can be present in modern and contemporary textile objects.

These studies will contribute to the expansion of scientific knowledge in the field of determining the pesticides present in modern and contemporary textile objects, but also to the substantiation of the performances of a new extraction, separation and detection method of these compounds.

The doctoral thesis is divided into two parts: **PART I – STUDY OF LITERATURE** and **PART II – PERSONAL CONTRIBUTIONS.**

PART I – STUDY OF LITERATURE includes 5 sub-chapters covering data related to:

Subchapter I.1. Types of textile fibres – brief history – Textile fibres classification as well as a brief history related to their appearance and use:

- natural vegetable fibres (cotton, flax, jute, coconut, etc.), animals (wool, mohair, etc. or from glandular secretion (filaments): silk) or minerals (e.g. asbestos - currently prohibited)
- chemical fibres – fibres obtained from natural or synthetic polymers by chemical means. Artificial fibres are produced from natural polymers (viscose, diacetate, rubber, etc.), and synthetic fibres are produced from synthetic polymers (polyamide, polyester, polyurethane, polyacrylonitrile, polypropylene, etc.)

Subchapter I.2. Types of modern and contemporary textile museum collections – The types of modern and contemporary textile museum collections that can be present in museums, historic houses, or private collections, structured as follows:

- Romanian traditional costumes
- Military uniforms: Military uniforms in the First World War, Military uniforms in the Second World War, Military uniforms in the post-war period and until today
- Uniforms in institutions of the Ministry of Internal Affairs

Subchapter I.3. Risks and good conservation practices in warehouses containing modern and contemporary textile museum collections – The main causes of the degradation of archaeological pieces, the methods of handling and also of storing costumes and textile materials[70].

Subchapter I.4. Pesticides – The main pests and the importance of knowing their biology and the environment in museums to be able to prevent pest attacks. Pesticide classification and physicochemical properties, brief history of pesticide use, as well as pesticide exposure and the main diseases associated with exposure.

Table 2. Classification according to toxicity, expressed as LD_{50} (mg/kg)[74]

Group	**Level of toxicity**	**LD_{50} * (mg/kg by weight of a laboratory mouse)**		**Label**
		Oral	Dermal	
I	extremely toxic	< 50	<50	red
II	strongly toxic	5-50	50-200	green
III	moderately toxic	50-2000	200-2000	blue
IV	low toxicity	<5000	-	black

*LD_{50} is the dose that causes the lethal effect in 50% of the animals in the test group.

Presentation of organic and inorganic chemicals identified as previously used in museum collections, as well as the selection of 3 pesticides malathion, methoxychlor and permethrin and some characteristic data of these substances.

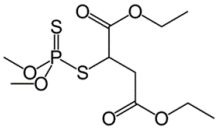


Figure 1. Malathion chemical structure (Source: File: Malathion.png - https://en.wikipedia.org)

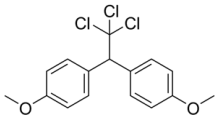


Figure 3. Methoxychlor chemical structure (Source: File: Methoxychlor chemical structure.png - https://en.wikipedia.org)

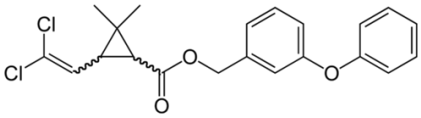
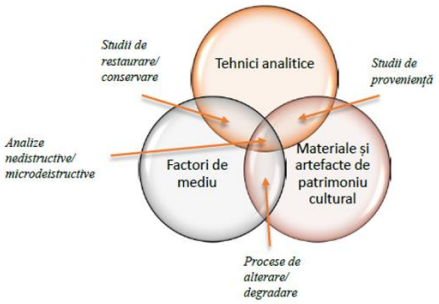


Figure 5. Permethrin chemical structure (Source: File: Permethrin-2D-skeletal.png - https://en.wikipedia.org

Table 4. Presentation of malathion, methoxychlor and permethrin [72]

Name	Class	Status and usage	Pests	Persistence
Malathion	Organophosphorus	Still used	Moths, beetles, crickets, silverfish	Low-moderate
Methoxychlor	Organochlorine	Still used. It has been banned in some countries since 2000	Moths, flies	High-moderate
Permethrin	Synthetic pyrethroid	Still used	Moths, beetles, crickets, silverfish	Low-moderate

Subchapter I.5. Pesticide extraction, separation, and detection methods – Some important research directions of extraction, separation, and detection methods of pesticides.



Description of the main extraction methods used for the analysis of pesticides, but also of other compounds from museum collections[140] and the presentation of the extraction method that was used in the experimental part: solid phase extraction on textile support - FPSE[142], a type of extraction that combines two extraction modes (SPME and SPE) in a single micro-extraction device, a unique concept that allows extraction to be performed while maintaining extraction performance characteristics such as robustness, specificity and efficiency.

Table 5. Preparation of FPSE (adapted from Kabir A. and Samanidou V.[146])

Stage I		**Stage II**		**Stage III**		
Preparing the fabric substrate [147,148]	→	**Preparing the sol-solution for coating the substrate [149]**	→	**Formation of sol-gel coatings on the fabric substrate**		
				Dip coating technology	**Aging, thermal conditioning and cleaning**	**Cutting FPSE[150]**
Nonpolar analytes – polyester fabric 100%		Sol-gel precursors: inorganic/organic modified		Coating the pretreated fabric with the sol-	Conditioning under helium gas flow,	Volume of sample<5mL – 1

		solution, typically 12h at room temperature	typically for 24h at 50ºC	cm diameter FPSE membrane
Polar analytes – hydrophilic fabric: 100% cotton cellulose	Inorganic/organic active polymer	Drying the coated FPSE membrane in air, typically for 1h.	Cleaning the FPSE membrane.	5mL<Volume of sample<20 mL – 2.5cm x 2.0 cm size of FPSE membrane
Clean and activate the fabric surface	Compatible solvent system			
	Acid catalyst and water			

Separation and detection techniques presented both individually and as complex systems for the evaluation of various chemicals present in museum collections. Among the techniques presented, gas chromatography coupled with mass spectrometry was used in the experimental part. In summary, GC/MS emerged as a robust technique for the organic analysis of art objects and has remained a standard tool for museums and cultural heritage laboratories to this day.

Table 8. Techniques for extraction, separation and detection of pesticides present in textile museum collections.

Sample	Extraction	Separation and detection	Pesticide	LOD	Reference
Karuk Tribe Artifacts	Swab with a cotton pad moistened with water	GC/MS	p-Dichlorobenzene	0,08 ng	[176]
Karuk Tribe Artifacts	Swab with a cotton pad moistened with water	GC/MS	Naphthalene	0,1 ng	[176]
Karuk Tribe Artifacts	Swab with a cotton pad moistened with water	GC/MS	DDT	0,2 ng	[176]
California Hoopa Tribe items	Solid-liquid extraction with methylene chloride	GC/MS	p-Dichlorobenzene	10 pg	[177]
California Hoopa Tribe items	Solid-liquid extraction with methylene chloride	GC/MS	Naphthalene	10 pg	[177]
California Hoopa Tribe items	Solid-liquid extraction with methylene chloride	GC/MS	DDT	10 pg	[177]
California Hoopa Tribe items	Solid-liquid extraction with methylene chloride	GC/MS	Lindan	10 pg	[177]
California Hoopa Tribe items	Solid-liquid extraction with methylene chloride	GC/MS	Thymol	10 pg	[177]
Wool fabric	Ultrasonic solid-liquid extraction with ethyl acetate:hexane (1:1)	GC/MS	77 pesticides	0,02–0,20 ppm	[178]
Cotton fabric	Ultrasonic solid-liquid extraction with ethyl acetate:hexane (1:1)	GC/MS	77 pesticides	0,02–0,20 ppm	[178]
Silk fabric	Ultrasonic solid-liquid extraction with ethyl acetate:hexane (1:1)	GC/MS	77 pesticides	0,02–0,20 ppm	[178]
Ramie fabric	Ultrasonic solid-liquid extraction with ethyl acetate:hexane (1:1)	GC/MS	77 pesticides	0,02–0,20 ppm	[178]
Cotton/polyester fabric	Ultrasonic solid-liquid extraction with ethyl acetate:hexane (1:1)	GC/MS	77 pesticides	0,02–0,20 ppm	[178]
Viscose-wool fabric	Ultrasonic solid-liquid extraction with ethyl acetate:hexane (1:1)	GC/MS	77 pesticides	0,02–0,20 ppm	[178]
Ecological textiles	SPME	GC/MS	Diazinon	0,03 ppb	[178]
Ecological textiles	SPME	GC/MS	Propetamphos	0,03 ppb	[178]
Ecological textiles	SPME	GC/MS	β-Chlorfenvinphos	0,03 ppb	[178]
Ecological textiles	SPME	GC/MS	Malathion	0,05 ppb	[178]
Māori raincoat		GC/MS	Naphthalene	7,1 ppm	[179]

	Swabbing with a cotton pad moistened with water, followed by extraction into ethyl acetate		Thymol	0,61 ppm	
			γHCH	<0,2 ppm	
			p,'p-DDE	0,078 ppm	
			Dieldrin	<1 ppm	
			p,'p-DDD	<0,5 ppm	
			p,'p-DDT	<1 ppm	
Māori cloak	Swabbing with a cotton pad moistened with water, followed by extraction into ethyl acetate	GC/MS	Naphthalene	2,7 ppm	[179]
			Thymol	0,61 ppm	
			γHCH	<0,2 ppm	
			p,'p-DDE	0,035 ppm	
			Dieldrin	3,1 ppm	
			p,'p-DDD	<0,5 ppm	
			p,'p-DDT	<1 ppm	
Tahiti mat	Swabbing with a cotton pad moistened with water, followed by extraction into ethyl acetate	GC/MS	Naphthalene	3,3 ppm	[179]
			Thymol	13 ppm	
			γHCH	<0,2 ppm	
			p,'p-DDE	0,095 ppm	
			Dieldrin	9,8 ppm	
			p,'p-DDD	<0,5 ppm	
			p,'p-DDT	<1 ppm	
Tahiti cloth	Swabbing with a cotton pad moistened with water, followed by extraction into ethyl acetate	GC/MS	Naphthalene	206 ppm	[179]
			Thymol	<0,5 ppm	
			γHCH	<0,2 ppm	
			p,'p-DDE	<0,03 ppm	
			Dieldrin	<1 ppm	
			p,'p-DDD	<0,5 ppm	
			p,'p-DDT	<1 ppm	
Tonga mat	Swabbing with a cotton pad moistened with water, followed by extraction into ethyl acetate	GC/MS	Naphthalene	1,6 ppm	[179]
			Thymol	<0,5 ppm	
			γHCH	<0,2 ppm	
			p,'p-DDE	<0,03 ppm	
			Dieldrin	<1 ppm	
			p,'p-DDD	<0,5 ppm	
			p,'p-DDT	<1 ppm	
Torres Strait Islander Mask	vapor phase sampling using sampling tubes loaded with Tenax-TA™	TD-GC-MS	Camphor	7,4 ng	[180]
			Naphthalene	10,7 ng	
			Thymol	8,4 ng	
			Chloro-naphthalene	12,0 ng	
			Dichlorvos	2,9 ng	
			Aldrin	52,6 ng	

PART II – PERSONAL CONTRIBUTIONS also consists of 5 subchapters and presents the experimental research carried out to obtain the integrated analytical system for the evaluation of modern and contemporary textile museum collections. The results obtained are summarized as follows:

Subchapter II.1. Optimizing the pesticides separation and quantification methods – Selection and optimization of the analysis method of the selected pesticides by testing 7 methods from the scientific literature, 2 solvents and 2 chromatographic columns. These tests were performed in the SCAN mode of the mass spectrometer and resulted in a specific but insufficiently sensitive method of analysis.

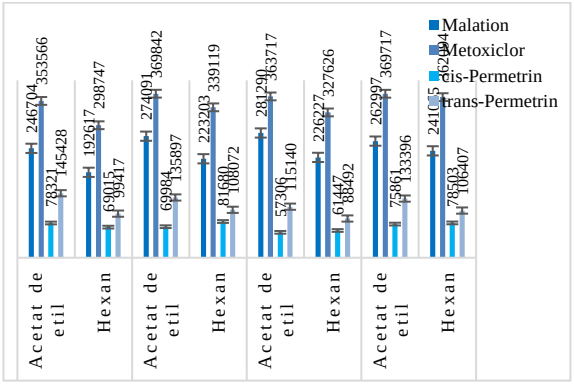


Figure 10. Graphic representation of the results obtained for DB-35MS column

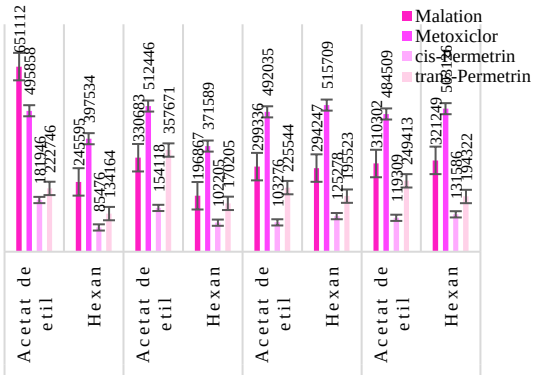
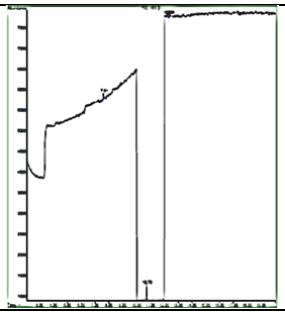
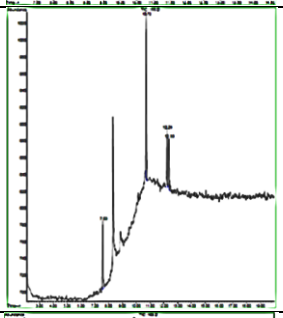
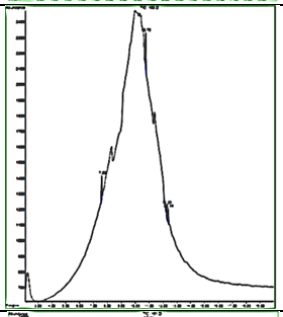
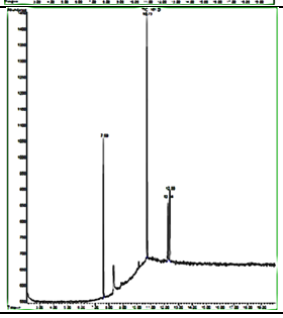


Figure 11. Graphic representation of the results obtained for ZB-5MSi column

In order to increase the sensitivity of the method, it was use the mass spectrometer in SIM (Selected Ion Monitoring) mode, which allows the collection of several points on a chromatographic peak, thus increasing the accuracy and precision of the quantitative results, thus establishing the method of separation and detection of pesticides: malathion, methoxychlor and permethrin.

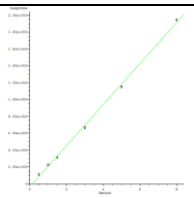
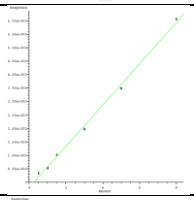
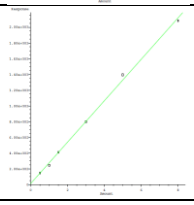
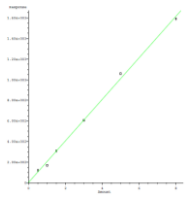
Table 12. Chromatograms obtained for the ZB-5MSi column

Method	Representative ions	Dwell (msec)	Chromatogram	Observation
Method 1	- group 1 – malathion: 32.10, 44, 47, 55.10, 63, 79, 93, 99, 125, 126, 127, 128, 131, 143, 158, 159, 173, 173.10 - group 2 – methoxychlor: 113.60, 114, 115, 152, 152.10, 153, 153.10, 169, 169.10, 195.10, 212, 212.10, 227, 227.10, 228, 238.10, 274.10, 274 - group 3 – permethrin: 44, 44.10, 51, 77, 89, 89.10, 91, 91.10, 127, 127.10, 163, 165, 168.10, 183, 183.10, 184, 184.10, 207	50		The chromatographic peaks obtained are well defined and can be separated and integrated. However, the main drawback of this method is that when the 3 groups are created, a "valley" (a change in the baseline) is created in the case of group 2 (methoxychlor)

Method 2	- malathion: 55.10, 63, 79, 93, 125, 127, 143, 158, 173, 173.10 - methoxychlor: 113.60, 152, 152.10, 169, 169.10, 212, 212.10, 227, 227.10, 228 - permethrin: 44, 44.10, 163, 165, 183, 183.10, 184, 184.10, 207	50		The chromatogram is defined, the compounds of interest can be integrated, but the aim is to obtain an optimal method, so the optimization continues with the decrease in the number of ions
Method 3	- malathion: 93, 99, 125, 158, 173 - methoxychlor: 152, 212, 227, 227.10, 228 - permethrin: 163, 165, 183, 183.10, 184.10	100		Decreasing the number of ions increases the sensitivity of the method, the peaks obtained being much better defined and separated from the baseline
Method 4	- malathion: 93, 125, 127, 173 - methoxychlor: 152, 212, 227, 228 - permethrin: 163, 165, 183, 184	200		The selected parameters are not suitable, so the dwell parameter is decreased to 50 msec
Method 5	- malathion: 93, 125, 173 - methoxychlor: 152, 227, 228 - permethrin: 163, 165, 183	50		The obtained chromatogram shows peaks separated from the baseline and well defined.

Subchapter II.2. Validation of the analysis method – In order to demonstrate the suitability of the proposed method, its validation was carried out by evaluating the performance parameters of the analytical method. The obtained results demonstrated a good separation of the analysed compounds, the selectivity of the method being evaluated by 3 methods. Also, the resulting precision, both at the level of repeatability and intermediate precision, was very good. The proposed analytical method allows both detection and quantification at the proposed concentration levels, the established working range is adequate for the proposed protocol, obtaining a correlation coefficient greater than 0.9900 for all 3 pesticides. The data series analysed shows a high degree of homogeneity, and the recovery percentage was 94.87% for methoxychlor, 95.87% for malathion, 98.27% for trans-Permethrin and 98.87% for cis-Permethrin.

Table 27. The calibration curve graph, the slope, and the correlation coefficient

Pesticide	Calibration curve graph	Correlation coefficient, r
Malathion		0,9990
Methoxychlor		0,9985
cis-Permethrin		0,9990
trans-Permethrin		0,9985

Subchapter II.3. Development and optimization of the extraction method – The development and optimization of the fabric phase sorptive extraction method (FPSE) was carried out by developing the extraction membrane and optimizing the method of obtaining it, but also the extraction process of selected pesticides both from solutions and from textile samples of laboratory constantly aiming to maximize the results obtained. Thus, the obtained fabric phase sorptive extraction consisted in making the extraction system composed of a polymer solution deposited on a textile substrate made of 100% cellulose. The sol-gel solution was obtained from 2.5 g polymer: polyethylene glycol (PEG) and PDMS, 2.5 mL trimethoxymethylsilane (MTMS), 5 mL solvent: methylene chloride:acetone (50/50 : V/V) and 1 mL trifluoroacetic acid 5% water. The polymerization time of the polymer solution on the textile substrate was set to 30 minutes at room temperature, followed by drying at 50°C in an oven with 20% ventilation in a standard atmosphere for 24 hours, washing the obtained membrane and drying again at 50°C, in an oven with 20% ventilation, in standard atmosphere, for 1 hour. An important aspect to mention is that an oven generally available in most laboratories and a standard atmosphere were used to obtain the extraction membrane, compared to the methods found in the literature, where drying is carried out in an "in-house" oven with an inert atmosphere – existing works use helium, an expensive gas with ever-increasing prices.

The extraction process of the selected pesticides was optimized to: 60 minutes in pesticide solution and 120 minutes in ethyl acetate for PEG, respectively an extraction of 120 minutes in pesticide solution and 120 minutes in ethyl acetate for PDMS.

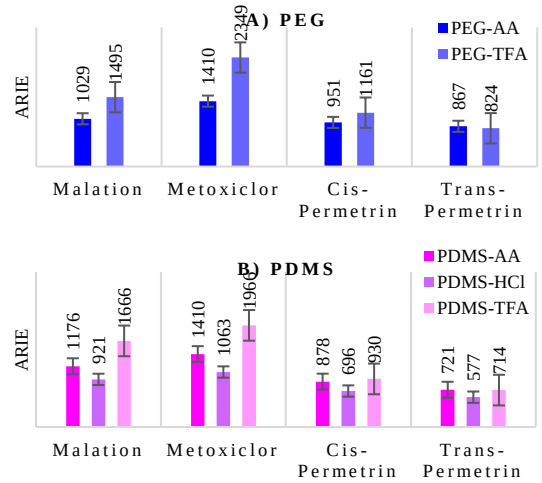


Figure 15. Graphic representation of the results obtained for the influence of the acid catalyst: a) PEG-FPSE, b) PDMS-FPSE

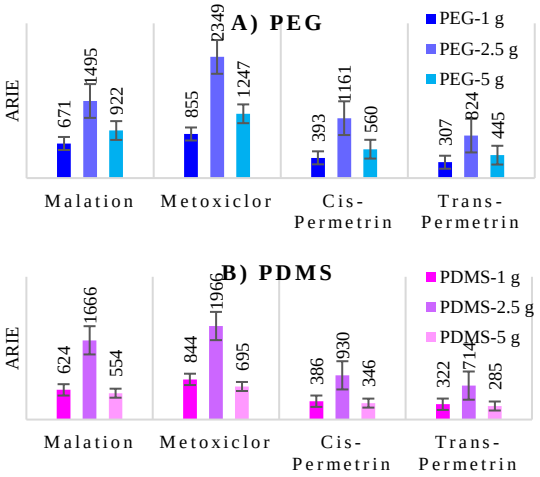


Figure 17. Graphic representation of the results obtained for the influence of the amount of polymer: a) PEG-FPSE, b) PDMS-FPSE

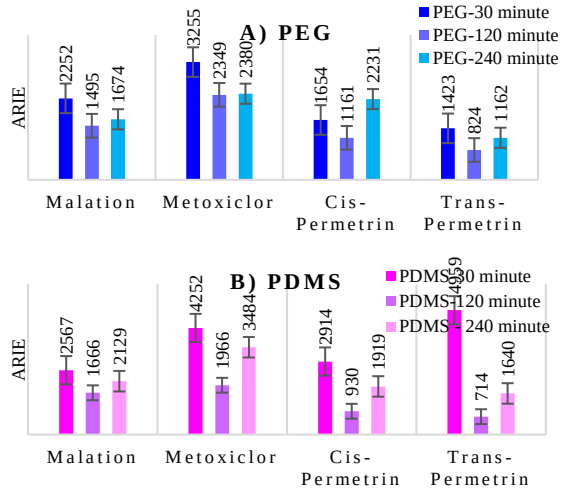


Figure 18. Graphic representation of the results obtained for the influence of the polymerization time: a) PEG-FPSE, b) PDMS-FPSE

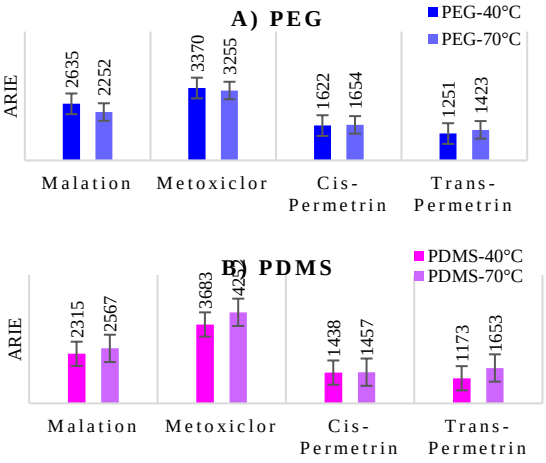
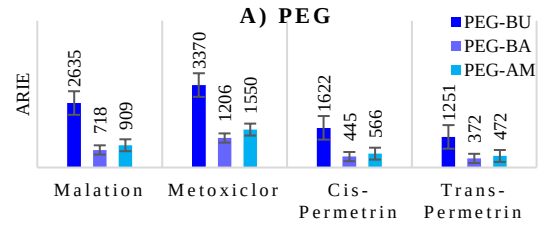
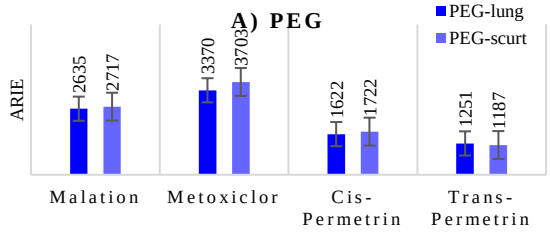


Figure 19. Graphic representation of the results obtained for the influence of ultrasonic bath temperature: a) PEG-FPSE, b) PDMS-FPSE





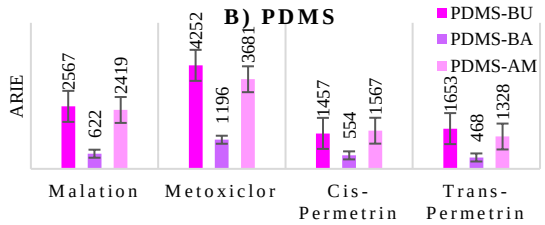


Figure 20. Graphic representation of the results obtained for the influence of the type of bath: a) PEG-FPSE, b) PDMS-FPSE

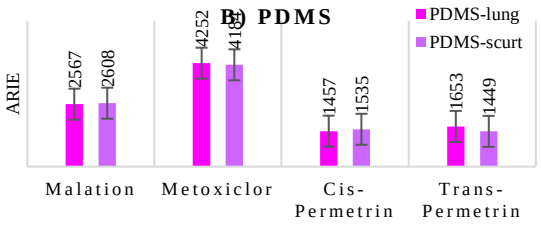


Figure 21. Graphic representation of the results obtained for the presence or absence of the last preparation steps: a) PEG-FPSE, b) PDMS-FPSE

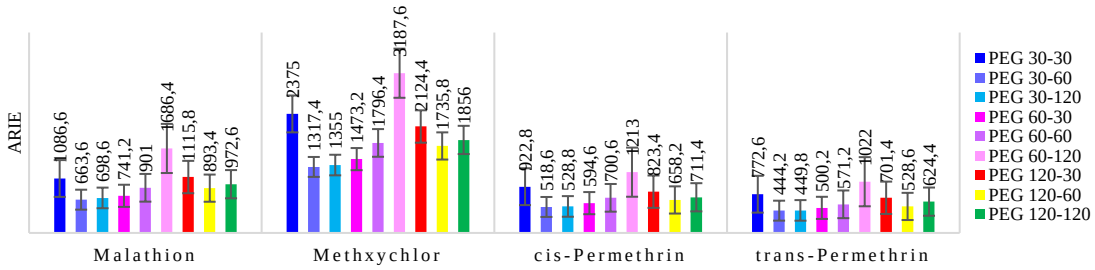


Figure 22. Graphic representation of the results obtained for the extraction time on PEG-FPSE and desorption time from PEG-FPSE in ethyl acetate

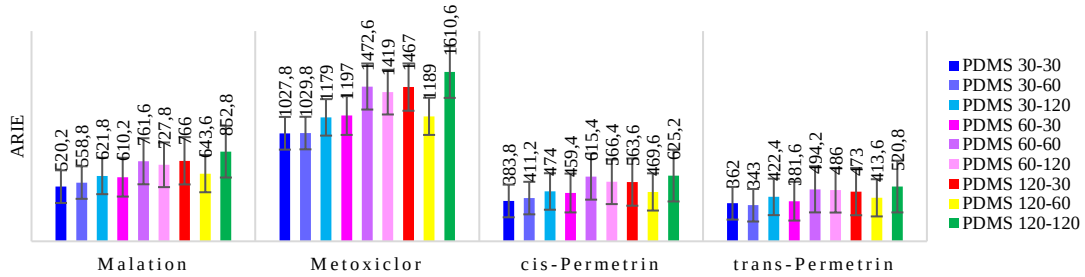


Figure 23. Graphic representation of the results obtained for the extraction time on PDMS-FPSE and desorption time from PDMS-FPSE in ethyl acetate

Also, for the laboratory textile samples, the extraction yields obtained indicated slightly increased values in the case of textile materials moistened with distilled water compared to those by direct contact, and the values obtained varied as follows:

- in PEG-FPSE case it varies from 59.333% (Wool-dry for the malathion compound) to 128.000% (Bbc/PES-wet for the trans-permethrin compound);
- in PDMS-FPSE case it varies from 52.667% (Bbc/PA-wet for the compound cis-permethrin) to 123.33 (Bbc-wet for the compound cis-permethrin).

Subchapter II.4. Statistical interpretation of experimental data – The statistical interpretation of the experimental data obtained for the optimization of the preparation method of fabric phase sorptive extraction was carried out by using the ANOVA - One Way [196], for which two hypotheses were issued: the null hypothesis (the values obtained are independent, without a significant difference) and the alternative hypothesis (the obtained values are dependent, with a significant difference). The confidence interval for which these hypotheses were assessed was 95%. For the results where the alternative hypothesis was accepted, the

Tukey test – Honestly significant difference – HSD[197] was used, for which the q_tukey value was determined by comparing the groups in pairs and related to the standardized q-critical value according to the number of groups and the degree of freedom. By using the two statistical tests, the working parameters were evaluated, correlated with the results in the previous subchapter "Development and optimization of the extraction method".

Subchapter II.5. Estimation of measurement uncertainty of the integrated analytical system for the evaluation of modern and contemporary textile museum collections – The estimation of the measurement uncertainty of the integrated system for the evaluation of modern and contemporary textile museum collections was conducted for the entire evaluation process of a possible museum textile sample. The identified sources of uncertainty were identified by an Ishikawa (cause-effect) diagram and quantified in standard, combined standard, relative standard, and percentage uncertainty for each analysed pesticide, considering a 95% confidence interval and a coverage factor k of 2. The uncertainty of the integrated analytical system for the assessment of modern and contemporary textile museum collections is 4.85% for methoxychlor, 5.50% for trans-permethrin, 5.78% for cis-permethrin and 8.39% for malathion.

Table 60. Calculated uncertainty

Compose standard uncertainty	**Expanded standard uncertainty**	
$U_{c_{malathion}} = 0.0419$	$U_{malation} = 2 \times U_{c_{malathion}} = 0.0839$ *	$\boldsymbol{U_{malathion}\% = 8.39\%}$
$U_{c_{methoxychlor}} = 0.0242$	$U_{metoxiclor} = 2 \times U_{c_{methoxychlor}} = 0.0485$ *	$\boldsymbol{U_{methoxychlor}\% = 4.85\%}$
$U_{c_{cis-permethrin}} = 0.0289$	$U_{cis-permetrin} = 2 \times U_{c_{cis-permethrin}} = 0.0578$ *	$\boldsymbol{U_{cis-permethrin}\% = 5.78\%}$
$U_{c_{trans-permethrin}} = 0.0275$	$U_{trans-permetrin} = 2 \times U_{c_{trans-permethrin}} = 0.0550$ *	$\boldsymbol{U_{trans-permethrin}\% = 5.50\%}$

** 95% confidence interval and a coverage factor k of 2*

ELEMENTS OF ORIGINALITY

The thesis includes the following new elements:

- Separation and detection of a mixture of three pesticides by gas chromatography coupled to mass spectrometry
- Two types of extraction membranes that can be used for solid phase extraction on textile support, the first containing PEG and the second PDMS
- Reducing the costs of obtaining the extraction membrane by replacing the "in-house" oven, which uses an inert atmosphere for drying, with an oven generally available in most laboratories - existing work uses helium, an expensive gas with increasingly expensive prices

- The first use of solid phase extraction on textile support as a non-destructive technique of textile museum collections
- The use of statistical methods for the interpretation of experimental data obtained for the optimization of the preparation method of solid phase extraction on a textile support
- o Obtaining an integrated analytical system for the assessment of modern and contemporary textile museum collections, composed of a non-destructive extraction technique of the analysed pesticides, followed by separation by gas chromatography and detection by mass spectrometry. This system presents, according to the list made by Lahanier and collaborators[7], the ideal characteristics to be applied in the analysis of heritage objects: non-destructive, fast, universal, versatile, sensitive and multi-elemental
- Proposing a method for estimating the measurement uncertainty of the analytical system obtained for the evaluation of modern and contemporary textile museum collections.

RESEARCH PERSPECTIVES

The technique proposed in the doctoral thesis "***Integrated analytical systems for the evaluation of modern and contemporary textile museum collections***" proved to be remarkably effective as a non-destructive tool for evaluating and quantifying the presence of pesticides in textile museum collections. The described approach reduces damage to heritage objects due to sampling compared to commonly used methods and may represent a starting point for future research to assess the compounds present in such samples.

ANNEXES

A1. LIST OF PUBLICATIONS PREPARED DURING THE PERIOD OF THE DOCTORAL THESIS

FI = 14,4

1. **Elena-Cornelia Mitran**, Irina-Mariana Săndulache, Lucia-Oana Secăreanu, Mihaela-Cristina Lite, Ovidiu George Iordache, Elena Perdum, Gabriel-Lucian Radu, Modern and contemporary textile museum collections: optimization method for pesticide analysis, UPB Scientific Bulletin, Series B, 2021, vol. 82, no. 3, pg. 191.

2. **Elena-Cornelia Mitran**, Irina-Mariana Săndulache, Lucia-Oana Secăreanu, Mihaela-Cristina Lite, Ovidiu George Iordache, Elena Perdum, Gabriel-Lucian Radu, Assessing the presence of pesticides in modern and contemporary textile artifacts using advanced analysis techniques, Industria Textilă, 2021, vol. 72, no.2, pg. 138, DOI: 10.35530/IT.072.02.1828. ***FI = 1,4***
3. **Elena-Cornelia Mitran**, Irina-Mariana Săndulache, Mihaela-Cristina Lite, Gabriel-Lucian Radu, Textile Museum Collections. SIM Method Validation for the Assessment of Pesticides, Materiale Plastice, 2021, vol. 58, no. 3, pg.1, https://doi.org/10.37358/Mat.Plast.1964 . ***FI = 0,8***
4. **Elena-Cornelia Tănăsescu**, Mihaela-Cristina Lite, Harmful health effects of pesticides used on museum textile artifacts – overview, Ecotoxicology and Environmental Safety, 2022, 247, 114240, https://doi.org/10.1016/j.ecoenv.2022.114240. ***FI = 6,8***
5. **Elena-Cornelia Tănăsescu**, Mihaela-Cristina Lite, Elena Perdum, Lucia-Oana Secăreanu, Ovidiu Iordache, Irina-Mariana Săndulache, Gabriel-Lucian Radu, Overview on the new generation of extraction technique: Fabric Solid-Phase Extraction, ICAMS 2022 – 9th International Conference on Advanced Materials and Systems Proceedings, 2022, pg. 517, https://doi.org/10.24264/icams-2022.V.8
6. **Elena-Cornelia Tănăsescu**, Alexandra-Gabriela Ene, Elena Perdum, Ovidiu Iordache, Gabriel-Lucian Radu, Anova and Tukey interpretation for FPSE innovative method applied in museum textiles, Industria Textilă, 2024, vol. 75, no.2, pg. 226, DOI: 10.35530/IT.075.02.20244. ***FI = 1,4***
7. **Elena-Cornelia Tănăsescu**, Alexandra-Gabriela Ene, Elena Perdum, Ovidiu Iordache, Lucia-Oana Secăreanu, New fabric phase sorptive extraction for nondestructive analysis of heritage textile samples, Heliyon, 2024, vol. 10, no.10, E31020, https://doi.org/10.1016/j.heliyon.2024.e31020. ***FI = 4,0***

A2. SCIENTIFIC COMMUNICATIONS

1. **Elena-Cornelia Tănăsescu**, Mihaela-Cristina Lite, Elena Perdum, Lucia-Oana Secăreanu, Ovidiu Iordache, Irina-Mariana Săndulache, Gabriel-Lucian Radu, Overview on the new generation of extraction technique: Fabric Solid-Phase Extraction, prezentare orală în cadrul Conferinței Internaționale ”ICAMS 2022 – 9th International Conference on Advanced Materials and Systems”, 2022.

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