MODERN AND CONTEMPORARY TEXTILE MUSEUM COLLECTIONS: OPTIMIZATION METHOD FOR PESTICIDE ANALYSIS

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The present work is focused on the optimization of an analytical method in order to obtain a suitable separation of three pesticides used in museum collections in order to prevent pest attack. A major inconvenient is their high toxicity that can affect museum`s staff health. In this paper, the pesticide analysis was optimized by varying 7 methods, 2 GC columns (ZB-5MSi and DB-35MS) and 2 solvents (ethyl acetate and hexane). The most satisfactory results were obtained when ZB-5MSi column and ethyl acetate were used. Future studies will continue with the extraction optimization and the validation of the final procedure.

Keywords: museum pesticides, GC-MS analysis, permethrin, malathion, methoxychlor

1. Introduction

There is no doubt about the importance of textile materials as a reflection of both present and past cultures. The archaeological materials offer plenty of information about ancient cultures, about the techniques of textile fabrics and about the correlation between these objects with their ceremonial and daily use. In many parts of the world, textile`s traditions have been passed forward from generation to generation. Examination of contemporary textile products provides an insight into the past so that it still amazes anyone who explores it.

Ethnographic textile pieces are complex, both from the perspective of the component materials, as well as from the techniques used to manufacture them. The act of preserving the cultural and artistic heritage is, first of all, a problem of scientific research and then a problem of technical execution.

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However, it is always necessary to consider any possible effects on the health of the staff that is directly involved in operations such as sampling, preserving or restoring the textile art objects.

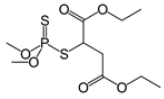
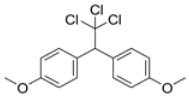
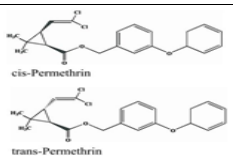
Over time, in order to protect textile objects from the attacks of pests, various toxic substances have been used. Pesticides and chemical compounds with complex structures are included in this category.

The aim of this paper is to establish a method of analysis of three pesticides which are used in museums and that can have negative effects on human health and on the environment. The selected pesticides are: malathion, methoxychlor and permethrin.

In Table 1 there are presented some historical data and the characteristics of these three selected pesticides. Fig. 1 illustrates the period of their use.

Table 1

Target pesticides characteristics

Name	Pesticide class	Status and use	Pests	Persistance
Malathion	Organophosphorus	It is still used	Moths, cockroaches, crickets, silverfish	Low to moderate
	Chemical Formulae		Structural Formulae	
	$C_{10}H_{19}O_6PS_2$			
Methoxychlor	Organochlorine	It is still used. In some countries since 2000 it has been banned	Moths, flies	Moderately to high
	Chemical Formulae		Structural Formulae	
	$C_{16}H_{15}Cl_3O_2$			
Permethrin	Synthetic pyrethroid	It is still used	Moths, cockroaches, crickets, silverfish	Low to moderate
	Chemical Formulae		Structural Formulae	
	$C_{21}H_{20}Cl_2O_3$			

The first pesticide used from the three mentioned above is methoxychlor, a pesticide that was first described in 1944, followed by malathion, that was firstly described in 1949 and patented in 1951. Regarding permethrin, this is a relatively new pesticide, first emerging in 1973 and then patented in 1976 [1].

2. Materials and Methods

The equipment used was an Agilent gas chromatograph with a mass spectrometer detector. The substances used were pestanal grade. To optimize the method, two types of solutions were prepared using ethyl acetate and hexane as solvent. The concentration of each solution was 100 ppm. For a better separation of the target compounds, two columns were selected: one from Phenomenex: ZB-5MSi and one from Agilent: DB-35MS.

Also, seven methods have been selected from which six are described in literature and adapted to the equipment used for analysis. The methods are shown in Table 2 below:

Table 2

The parameters of the selected methods

Method	Injection volume/ gas flow	Injector temp.	Temperature programme	Auxiliary temp.	Scan range
1 [2]	1µl/ 1 ml/min	200ºC	100ºC - 1 min 100ºC to 150ºC with 25ºC / min 150ºC - 1 min 150ºC to 260ºC with 5ºC / min 260ºC - 3 min	200ºC	30 – 400
2 [3]	1µl/ 1 ml/min	200ºC	60ºC - 5 min 60ºC to 250ºC with 25ºC / min 250ºC - 5 min	200ºC	50 – 300
3 [4]	1µl/ 1 ml/min	250ºC	75ºC - 3 min 75ºC to 120ºC with 25ºC / min 120ºC to 300ºC with 5ºC / min 300ºC - 11 min	300ºC	30 – 400
4 [5]	1µl/ 1 ml/min	310ºC	40ºC - 2 min 40ºC to 250ºC with 12ºC / min 250ºC - 2 min	280ºC	29 – 420
5 [6]	1µl/ 1 ml/min	280ºC	92ºC - 2.5 min 92ºC to 175ºC with 15ºC / min 175 ° C - 13 min 175ºC to 280ºC with 20ºC / min 280ºC - 3 min	290ºC	30 – 400
6 [7]	1µl/ 1.2 ml/min	270ºC	50ºC - 1 min 50ºC to 180ºC with 30ºC / min 180ºC - 1 min 180ºC to 280ºC with 15ºC / min 280ºC - 20 min	280ºC	30 – 400
7*	1µl/ 1.2 ml/min	300ºC	130ºC to 280ºC with 15ºC / min 280ºC - 10 min	300ºC	30 – 500

* Optimized method in our laboratory for another study on permethrin

3. Results and discussion

The results obtained when using the two chromatographic columns and the two selected solvents are presented in Table 3 and Table 4.

Table 3

Interpretation result for each method used on DB-35MS column

DB-35MS		
	Ethyl acetate	Hexane
Method 1	Chromatographic peaks are obtained for malathion and methoxychlor (but the peak for methoxychlor does not come out completely). The analysis time is insufficient for all compounds.	The behavior of the compounds using hexane is similar for each method with ethyl acetate.
Method 2	A single chromatographic peak is obtained for malathion. The analysis time is insufficient for all compounds.	
Method 3	Chromatographic peaks are obtained for all three compounds. In the case of permethrin, the split of the compound in 4 chromatographic peaks can be observed.	
Method 4	A single chromatographic peak is obtained for malathion. The analysis time is insufficient for all compounds.	
Method 5	Chromatographic peaks are obtained for all three compounds, but they are present at the end of the chromatogram, which means that the parameters selected for the beginning part of the method are not adequate. Permethrin is separated into two peaks, one representing the cis isomer, the other being the trans isomer.	
Method 6	Chromatographic peaks are obtained for all three compounds. As in the case of method 5, permethrin is separated into the two cis and trans isomers.	
Method 7	Chromatographic peaks are obtained for all three compounds. As with method 5 and 6, permethrin is separated into the two cis and trans isomers.	

Table 4

Interpretation result for each method used on ZB-5MSi column

ZB-5MSi		
	Ethyl acetate	Hexane
Method 1	Chromatographic peaks are obtained for all three compounds, but the method is not suitable for the column because it generates a "leak" (we can observe on	Chromatographic peaks are obtained for all three compounds, but the appearance of the two isomers of permethrin at the end of the

	the chromatogram compounds from the composition of the stationary phase: siloxanes)	chromatogram confers an image of "unfinished chromatogram".
Method 2	A single chromatographic peak is obtained for malathion. The analysis time is insufficient for all compounds.	No compound is obtained from the three pursued.
Method 3	Chromatographic peaks are obtained for all three compounds. Permethrin is separated into two peaks, one representing the cis isomer, the other being the trans isomer. The method is not beneficial for the column, as it determines its "leak".	Chromatographic peaks are obtained for all three compounds. Permethrin is separated into two peaks, one representing the cis isomer, the other being the trans isomer.
Method 4	No compound is obtained from the three pursued.	A single chromatographic peak is obtained for malathion. The analysis time is insufficient for all compounds.
Method 5	Chromatographic peaks are obtained for all three compounds, but they appear at the end of the chromatogram. Permethrin is divided into three peaks. Analysis time is insufficient.	The behavior of the compounds using hexane is similar with ethyl acetate.
Method 6	Chromatographic peaks are obtained for all three compounds. As with method 3, permethrin is separated into the two cis and trans isomers.	The behavior of the compounds using hexane is similar with ethyl acetate.
Method 7	Chromatographic peaks are obtained for all three compounds. When using method 3 and 6, permethrin is separated into the two cis and trans isomers.	The behavior of the compounds using hexane is similar with ethyl acetate.

The results obtained on the DB-35MS column (Fig.1) reveals that:

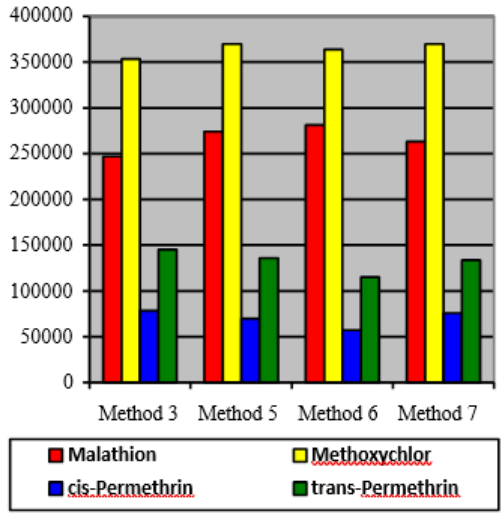
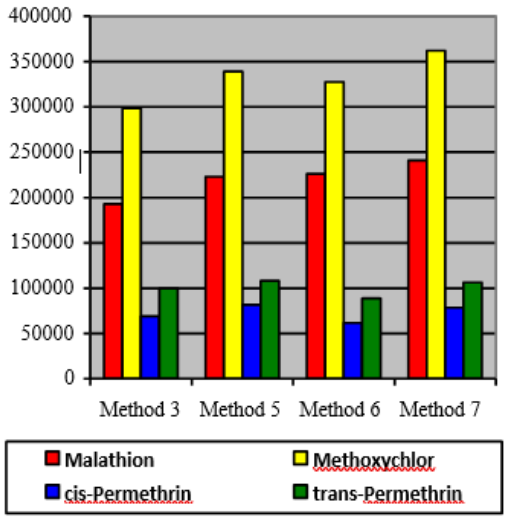
1. For malathion the best determination method was method 6, which uses ethyl acetate as solvent;

2. For methoxychlor the most suitable method of determination was method 5 (ethyl acetate as solvent), but also method 6 (ethyl acetate as solvent) or method 7 (ethyl acetate as solvent;

3. For permethrin, two peaks were obtained, representing cis and trans isomers. For the cis isomer, a larger area was obtained for method 3 (ethyl acetate as solvent) and method 5 (hexane as solvent). For the trans isomer, larger areas were obtained when using method 3 (ethyl acetate as solvent), but also in methods 5 and 7 (ethyl acetate as solvent).

Table 5

Results obtained on DB-35MS column

Ethyl acetate	Hexane
	
The areas of the 3 compounds (malathion, methoxychlor and permethrin - cis and trans) obtained using method 3, 5, 6 and 7 are represented above. Only 4 methods were chosen to be represented due to the presence of all 3 compounds of interest. In the case of method 3, only the areas of the cis and trans isomers (those appearing in the other methods) were added to the graph.	As it can be seen from the results presented above, the separation of the compounds does not depend on the solvent used, Which denotes the fact that the separation of the three compounds takes place in a similar way for each method used. The difference appears when quantifying the resulting areas. The graphical representation of the obtained areas was performed as in the case of ethyl acetate samples, the selection of the represented methods being performed according to the existence of the compounds of interest

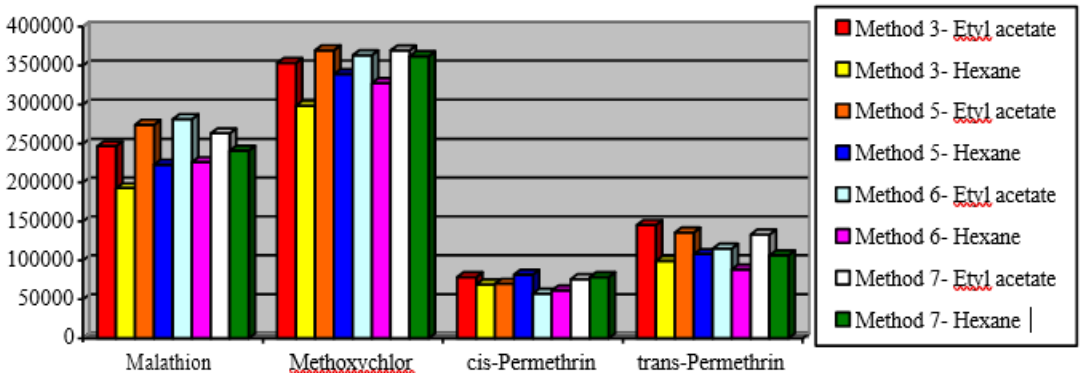
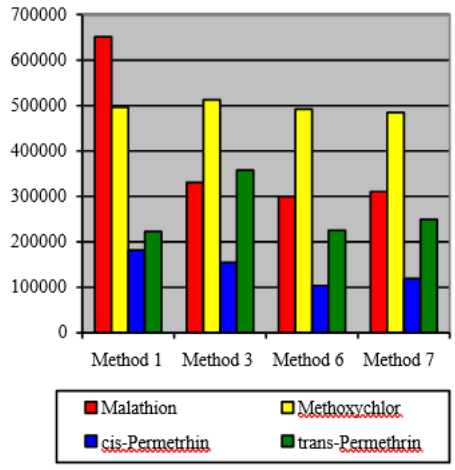
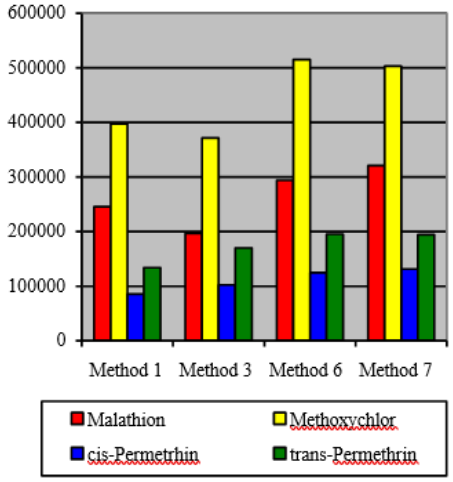


Fig. 1. Graphic representation of the DB-35MS column results

Table 6

Results obtained on ZB-5MSi column

Ethyl acetate	Hexane
	
In the figure above, the areas of the 3 compounds (malathion, methoxychlor and permethrin - cis and trans) obtained using methods 1, 3, 6 and 7 are represented. Like in the case of DB-35MS column, only these 4 methods were chosen to be represented, due to the presence of all 3 compounds of interest.	The separation of the target compounds is similar for both types of solvent used. The difference appears when quantifying the resulting areas. The graphical representation of the obtained areas was performed as in the case of ethyl acetate samples; the selection of the represented methods has been made according to the existence of the compounds of interest.

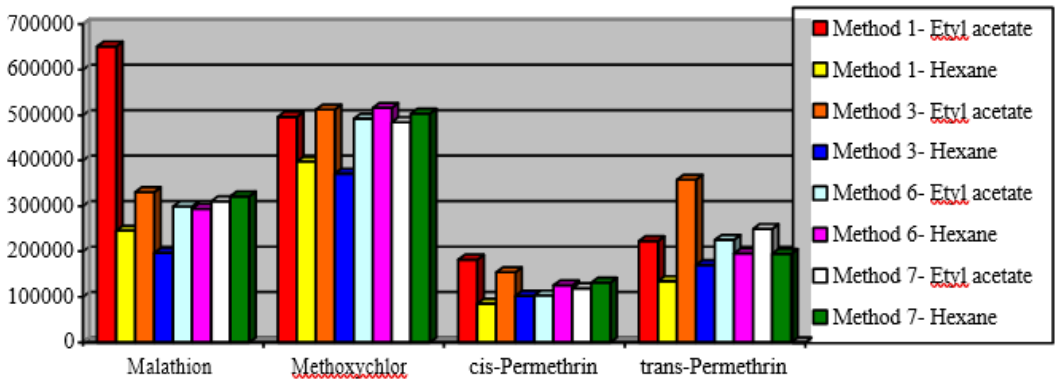


Fig. 2. Graphic representation of the ZB-5MSi column results

The results obtained on ZB-5MSi offer the following information:

1. For malathion, the most efficient method to determine the pesticide was method 1, with ethyl acetate as solvent;
2. For methoxychlor, the best determination method was method 6, using hexane as solvent. Method 3, with ethyl acetate as solvent, may also be used;

3. For permethrin, two peaks are obtained, representing cis and trans isomers. For the cis isomer, a better area was obtained for method 1. In the case of the trans isomer, better areas were obtained when using method 3, ethyl acetate solvent. In addition to the above statements, it should be mentioned that even if method 1, which uses ethyl acetate as solvent, is suitable to determine malathion, this method is actually very harmful for the column, as its stationary phase is affected (the chromatogram presents peaks assigned to the compounds from its structure: siloxanes).

4. Conclusions

By comparing the results obtained it can be concluded that the most satisfactory results were acquired when using the ZB-5MSi column (larger areas, higher peaks). From the perspective of the solvent used, it was determined that ethyl acetate can be used in future studies to separate the three selected pesticides. The study will be continued with the validation of the analysis method and the optimization of an extraction method to determine the three selected pesticide.

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