

Assessing the presence of pesticides in modern and contemporary textile artifacts using advanced analysis techniques

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ABSTRACT – REZUMAT

Assessing the presence of pesticides in modern and contemporary textile artifacts using advanced analysis techniques

The examination of contemporary textiles continuously offers amazing perspectives of the past for anyone who explores them. The ethnographic textile pieces are complex, both from the perspective of the component materials and regarding the techniques used for their manufacture. The action of conserving the cultural and artistic patrimony is firstly a matter of scientific research and then of technical execution. However, the possible health effects on the personnel, which are directly involved in the actions of sampling, conservation or restoration of the textile art objects, must always be taken into consideration. Textile objects can be contaminated with various toxic residues (e.g., pesticides). When investigating archaeological, modern and contemporary textiles it is very important to maintain the integrity of the artifacts, as they cannot be replaced, and the consumption or damage of even a small part of them for analytical purposes should be undertaken only if the data cannot be obtained differently. For determining the presence of pesticides in the samples they must be subjected to processes such as: extraction, enrichment of samples, isolation, identification, and quantification.

Given the above, the most common methods of extraction and determination of pesticides present in textile artifacts were briefly discussed. Punctually, the analytical techniques used in the case of three selected pesticides (malathion, methoxychlor and permethrin) were evaluated.

Keywords: GC-MS, SPME, malathion, methoxychlor, permethrin

Evaluarea prezenței pesticidelor în artefactele textile moderne și contemporane prin utilizarea tehnicilor analitice avansate

Examinarea produselor textile contemporane oferă perspective asupra trecutului într-un continuum care uimește pe oricine îl explorează. Piese textile etnografice sunt complexe, atât din punctul de vedere al materialelor componente, cât și din acela al tehnicilor folosite pentru realizarea lor. Acțiunea de conservare a patrimoniului cultural și artistic este în primul rând o problemă de cercetare științifică și apoi de execuție tehnică. Însă, trebuie luate în considerare întotdeauna eventualele efecte asupra sănătății personalului implicat direct în acțiunile de prelevare, conservare sau restaurare a obiectelor textile de artă. Obiectele textile pot fi contaminate cu diferite reziduuri toxice (de exemplu pesticide). În cazul analizei materialelor arheologice, moderne și contemporane este foarte importantă păstrarea intactă a artefactelor, întrucât acestea nu pot fi înlocuite, iar consumul sau deteriorarea chiar și a unei mici părți a acestora în scopuri analitice trebuie să fie întreprinsă numai în cazul în care datele nu pot fi altfel obținute. În vederea determinării prezenței pesticidelor în probele pe care dorim să le analizăm, acestea trebuie să treacă prin procese precum: extracție, îmbogățirea probelor, izolarea acestora, identificarea și cuantificarea acestora.

Având în vedere cele menționate anterior, în continuare s-a discutat pe scurt despre cele mai frecvent utilizate metode de extracție și determinare a pesticidelor prezente în artefacte textile, dar și punctual, prin evaluarea tehnicilor analitice utilizate în cazul a trei pesticide selectate: malation, metoxiclor și permethrin.

Cuvinte-cheie: GC-MS, SPME, malation, metoxiclor, permethrin

INTRODUCTION

Undoubtedly, textiles are a reflection of both present and past cultures. The possible effects on the health of the personnel, which are directly involved in the sampling, conservation or restoration of the textile art objects, must always be considered.

The quality of the air (temperature, humidity, light, fungal contamination) can influence the textile materials exposed in museums, as well as the human

health [1, 2]. Textiles can be contaminated with various toxic residues (e.g., pesticides). Pesticides are chemical compounds used to remove pests. They can enter the pest's body through their skin, mouth or airways.

Pesticides can have both natural and synthetic origin. Also, in the class of pesticides, hormonal regulators that inhibit the maturation of insects are sometimes mentioned.

Within museum collections, different types of pesticides or fumigants have been used over time, about which not much is known. Thus, they became dangerous even for humans, when coming into contact with textiles treated with such substances.

It is very important to use advanced techniques for identifying/quantifying these hazardous substances in order to develop protection plans for museum staff. Over time, scientists have tried to develop and optimize such analysis techniques. This paper proposes to review the main analytical procedures for identifying and quantifying the pesticides that may be present in modern and contemporary textiles.

GENERAL METHODS

Frequently, the analytical method is preceded by a process of extraction of the analyte of interest. Liquid-liquid extraction (LLE) is a common extraction method based on the different solubility of chemicals in two different liquid solvents [3]. Two phases will be formed: an aqueous phase (in which water-miscible compounds will be separated) and an organic phase (in which the pesticides will be extracted). The first successful commercial liquid-liquid extraction operation was developed for the oil industry in 1909, when Edeleanu's process was used to remove aromatic hydrocarbons from kerosene, using liquid sulfur dioxide as solvent [4]. However, this type of method is less used for the analysis of environmental samples, due to high solvent consumption and low recovery rates [3].

Another common extraction is solid-liquid extraction (SLE). The process consists in extracting the compounds of interest from a solid sample with a suitable solvent.

Supercritical Fluid Extraction (SFE) is a method that processes both solid and semi-solid samples. The difference between SFE and SLE is that, in the case of SFE, the extraction solvent is a supercritical fluid. The first recognition of the analytical potential of supercritical fluids probably came in a note made by James Lovelock in 1958 [5]. However, the first supercritical chromatographic separation was reported in 1962 by Klesper [6].

A very commonly used extraction method in the case of heritage samples is solid-phase micro-extraction (SPME)-absorption/desorption technique. The principle consists in immersing a fiber covered with silica in the sample. SPME was introduced in 1989 and it attracts more and more attention due to its simplicity and ease of use [7–9]. The sample can either be directly desorbed from the fiber in a chromatographic injection port or it can be desorbed from the fiber using a solvent [10]. Both methods have been used in various studies for pesticide analysis [11–16].

Solid phase micro-extraction in combination with gas chromatography coupled with mass spectrometry (GC-MS) offers a simple and sensitive option for analyzing art textiles that are contaminated with volatile or semi-volatile organic pesticides [17].

Liquid-liquid dispersant micro-extraction (DLLME) is also a technique that is sometimes used to analyze contaminants in heritage samples. This technique consists in dissolving a water-insoluble extract in a water-miscible solvent, followed by centrifugation of this mixture. By centrifugation, the contact surface between the phases increases, achieving a faster extraction, compared to the liquid-liquid extraction [18, 19].

A relatively new extraction technique is one-drop micro-extraction (SDME) – a miniaturized solvent micro-extraction technique. In this type of extraction, a single micro-drop of organic solvent suspended at the tip of the micro-syringe needle is used and the sample solution can be pre-concentrated directly by D-SDME (direct SDME) or by SDME headspace (HS-SDME) [20].

One of the most common methods for determining pesticides is QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe). The name of this procedure comes from its advantages: fast, easy, cheap, efficient, robust and safe. It consists of extracting the analyte with an organic solvent, removing the water and analyzing by a suitable technique [10].

The most used methods for the analysis of toxic substances in textiles are liquid chromatography coupled with mass spectrometry (LC-MS) [21] and gas chromatography coupled with mass spectrometry (GC-MS) [21, 22–25]. GC-MS is a widely used method due to the ability to combine both the retention time of each analyte and the correct matching of the library with reference mass spectra, which provides a high degree of certainty for identification. The use of a spectrometric mass detector also allows the identification of unexpected pesticides or possible degradation products. In a study conducted in 2017 by Salmo and his collaborators on nine artifacts belonging to the Karuk Tribe, they identified 3 types of pesticides: p-dichlorobenzene, naphthalene and DDT [2].

Palmer et al. analyzed 17 heritage objects belonging to the Hupa Tribe of California and identified the presence of 5 pesticides: p-dichlorobenzene, naphthalene, thymol, lindane and DDT [27]. Another type of detector used in GC analysis is the flame ionization detector (FID). Glastrup was one of the first researchers to use GC-FID to analyze pesticides in modern and contemporary heritage samples [28].

Direct analysis by real-time mass spectrometry (DART-MS) is a method that allows the analysis of solid samples without the need for prior preparation and can be used to determine substances known to have a negative effect on human health and which may be present in textiles [29, 30].

Once a method for determining the pesticides has been established and implemented, any subsequent analysis of a sample can be completed in less than one hour and modern data systems can be used to automate the identification and quantification of compounds.

PESTICIDE ASSESSMENT VIA GC-MS – MALATHION, METHOXYCHLOR AND PERMETHRIN

In order to exemplify a pesticide assessment method three pesticides were subjected to GC-MS analysis: malathion, methoxychlor and permethrin.

The chronological evolution of the three selected pesticides is shown in figure 1 and their chemical structures are presented in table 1.

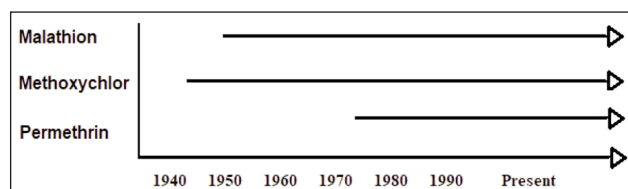


Fig. 1. Chronological evolution of the three pesticides [31]

Malathion is a compound from the class of organophosphate pesticides and it is found in liquid form, colorless or at most up to amber color, with a smell similar to garlic [32].

Physical-chemical properties:

- vapour pressure [33]: 1.78×10^{-4} mmHg at 25°C or 5.3 mPa at 30°C; also 1.2×10^{-4} to 8×10^{-6} mmHg at 20°C;

- water-octanol partition coefficient (log KOW) [34]: 2.75, 2.36–2.89;

- molecular weight [35]: 330.4 kg/kmol;

- water solubility [35]: 145 mg/l.

Malathion is toxic, thus it is recommended to avoid exposure through inhalation, skin contact or ingestion [35]. The exposure of humans to malathion can give various symptoms such as excessive sweating, pupil contraction, tearing, salivation, abdominal cramps, diarrhea, vomiting, changes in blood pressure (rapid increase or decrease of the heart rate), headache, insomnia [36–38]. Exposure to high doses of malathion can lead to the development of Intermediate Syndrome, which is manifested by acute coronary insufficiency, pre-infarction etc. [39, 40].

Some regulations and recommendations for malathion include the following [42]:

- Occupational Safety and Health Administration (OSHA) has set an occupational malathion exposure limit of 15 mg/m^3 for a working day of 8 hours, 40 hours per week. National Institute for Occupational Safety and Health (NIOSH) recommends that workers should not be exposed to more than 10 mg/m^3 malathion on a working day of 10 hours, 40 hours per week. NIOSH also recommends that a level of 250 mg/m^3 of malathion in the air can be considered immediately dangerous to life and health.
- The Food and Drug Administration (FDA) and the Environmental Protection Agency (EPA) allow a maximum of 8 ppm of malathion to be present as residues on specific crops used as food.

Methoxychlor is an organochlorine pesticide, in the form of pale yellow powder with a slightly fruity or musty smell [42].

Physical-chemical properties:

- vapour pressure [43]: 5.56×10^{-3} Pa at 25°C;

- water-octanol partition coefficient (log KOW) [45]: 5.67;

- molecular weight: 345.65 kg/kmol;

- water solubility [43]: 0.302 mg/l at 25°C.

Methoxychlor is a pesticide proven to be an endocrine disruptor [44].

EPA limits the amount of methoxychlor that may be present in drinking water to 0.04 parts of methoxychlor to one million parts of water (0.04 ppm). The EPA has also set limits of 1–100 ppm on the amount of methoxychlor that may be present in various agricultural products (fruits, vegetables, grains, meat, milk and animal food). FDA limits the amount of methoxychlor in bottled water at 0.04 ppm. The EPA restricts the amount of methoxychlor that can be released into the environment during combustion or by disposal in landfills. OSHA has set Permissible Exposure Limit (PEL) of 15 mg/m^3 of air to the average amount of methoxychlor that may be present in the air during a working day of 8 hours [45].

Table 1

| STRUCTURE OF THE THREE SELECTED PESTICIDES | | |
|--|--------------|--|
| Malathion | Methoxychlor | Permethrin (cis and trans-isomer) |
| | | cis-Permethrin trans-Permethrin |

Permethrin is a pyrethroid pesticide. Permethrin is a mixture of two stereoisomers (cis- and trans-permethrin) [46]. Permethrin varies in appearance, from a colorless crystal to a yellowish or brown viscous liquid [46, 47].

Physical-chemical properties:

- vapour pressure [47]: 2.15×10^{-8} mmHg;
- water-octanol partition coefficient (log KOW) [21]: 6.1;
- molecular weight: 391.3 kg/kmol;
- water solubility [46, 47]: 5.5×10^{-3} mg/l, 6×10^{-3} mg/l.

Permethrin causes damages to the nervous system of insects. It interferes with sodium channels to disrupt the function of neurons and causes muscle spasm, culminating in paralysis and death [48, 49].

The World Health Organization (WHO) recommended that the level of permethrin in drinking water should not exceed 20 µg/l. OSHA has set a level of pyrethroids in the air at work. Occupational exposure limits for a working day of 8 hours and 40 hours of work per week are 5 mg per cubic meter (mg/m^3). The EPA has recommended daily oral exposure limits for 10 different types of pyrethroids. These limits are between 0.005 and 0.05 mg/kg/day [48].

Due to the many negative effects on humans and the environment, it is important and still necessary to develop precise, sensitive and robust extraction and analysis methods to determine the amount of pesticides and to maintain them in accordance with the laws. Considering all these aspects, the most commonly used method for the extraction and determination of the three pesticides of interest was briefly discussed below.

In general, sampling techniques mostly involve swab of wipe-based surface sampling or removing a portion of the object.

GC-MS is one of the most widely used analytical methods for the analysis of organic compounds at the trace level. The MS detector ensures excellent sensitivity, the LODs frequently having values close to the picogram (10^{-12} grams) [49]. Unlike TCD (Thermal Conductivity Detector), FID (Flame Ionization Detector) and ECD (Electron Capture Detector), wherein a peak from the resulting chromatogram simply indicates a response to a particular compound exiting the column, the MS detector provides three dimensions of information: the m/z ratio, the intensity and the retention time.

Zhou et al. developed a method for the determination of 77 pesticides from textile materials by GC-MS. They analyzed a mixture of 12 pyrethroids (including permethrin), 26 organochlorines (including methoxychlor), 30 organophosphorus (including malathion), 8 carbamates and an organic nitrogen pesticide [50].

Another method for determining organophosphorus pesticides in textiles was proposed by Hu et al. They used solid phase microextraction (SPME) and GC as the method of analysis. Malathion was among the pesticides analyzed. The detection limit for the 11 selected pesticides was in the range of 0.03 µg/l – 0.5 µg/l [51].

18 objects from the Cook-voyage collections at the Pitt Rivers Museum, University of Oxford were analyzed by GC-MS for the evaluation of pesticide residues (including permethrin) by Charlton et al. [52]. The sampling method used by them was swab surface sampling: they used cotton pads moistened with distilled water and evaluated how appropriate this method is. They chose this procedure because water is considered to be the only safe solvent to use, but a disadvantage is that most pesticides have low solubility in water. These cotton pads (35–40 pads taken) were weighed and extracted with ethyl acetate. The resulting solutions were analyzed by GC-MS.

Rushworth et al. [53] developed a new method of sampling and a non-invasive analysis to assess the volatile pesticides that may be present in heritage collections. They performed a vapor phase sampling using sampling tubes loaded with Tenax-TA™, capturing the analytes in these tubes. Subsequently, they performed the analysis of the resulting vapors using thermal desorption coupled with GC-MS (TD-GC-MS). Another innovative method is the analysis of pesticides from aqueous samples by using a sampling device coupled with GC-MS [54].

Advanced analytical methods and techniques are an essential tool in the field of cultural heritage, as they provide the means to understand the studied objects [55, 56].

CONCLUSIONS

There is a major necessity of precise, selective and reproducible analytic techniques for evaluating and quantifying the presence of pesticides in modern and contemporary textile artifacts. The general methods for assessing the presence of pesticides in textile materials and specific methods for three types of pesticides which have been used to treat textiles against the attack of pests have been presented in this paperwork.

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