**MATERIALE PLASTICE**
*https://revmaterialeplastice.ro*
*https://doi.org/10.37358/Mat.Plast.1964*

# Textile Museum Collections. SIM Method Validation for the Assessment of Pesticides

**ELENA-CORNELIA MITRAN[1,2*], IRINA-MARIANA SANDULACHE[1], CRISTINA-MIHAELA LITE[1,2], LUCIAN GABRIEL RADU[2]**

[1]National R&D Institute for Textiles and Leather Bucharest, 16 Lucretiu Patrascanu, 030508, Bucharest, Romania
[2]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061, Bucharest, Romania

***Abstract:*** *In time the environmental conditions could damage textiles (materials/ artifacts) causing the need to develop better non-destructive or at least micro-destructive analysis techniques of the samples. There are ethnographic textile artifacts that were treated in the past with various pesticides, that have not been mentioned in any document. These are often re-treated with chemicals by museum staff as a method of preventing pest infestation. Due to the progressive use of many pesticides, this paper was focused on the detection and quantification of three pesticides: malathion, methoxychlor, and permethrin (cis- and trans- isomers). Gas chromatography is one of the most widely used analytical techniques for characterizing volatile organic compounds and therefore was the analytical method of choice for the present study. Because these analytes are found at trace levels, the detection and quantification limits of analytes are very small and it is necessary to optimize and validate a SIM method - that allows the mass spectrometer to detect specific compounds with high sensitivity. In SIM mode, the instrument is set to collect data at selected masses of interest, thus increasing the accuracy and precision of the quantitative results. The present paper is aimed to develop this type of method with specificity and selectivity, high precision (expressed in terms of repeatability and intermediate accuracy), accuracy, suitable working range and linearity, and high degree of series' homogenity.*

***Keywords****: SIM method, gas-chromatography, pesticide, textile*

## 1. Introduction

From a chemical perspective, both natural and artificial fibers (except asbestos, glass and metal fibers) are polymeric materials, consisting of repetitive structural (or monomer) units. Some fibers are homopolymers, for example cellulose, a natural fiber consisting of only 3-D-glucose units. Nylon 6, Nylon 11, polyethylene, polypropylene, polyvinyl chloride and polyacrylonitrile are examples of synthetic homopolymers that can be spun into fibers. Heteropolymers are formed by the co-polymerization of two or more different monomers. This class includes protein fibers, which can be constituted of 20 different amino acids. Nylon 66, polyesters and modacrylic fibers are also classic examples of heteropolymers.

The chronological history of man-made textile fibers and yarns can be listed as following [1]:

1) The 1889–1930s: emergence of processes for creating filament yarns based on natural polymers (e.g., cellulose-based yarns, also known as vegetable silk) [2,3].

2) The 1930s–1940s: based mainly on the production of short fibers (cotton type and wool type). This is also the timeframe when the first synthetic fibers were developed (i.e., neoprene [4], nylon [5], polyurethane [6], polyacrylonitrile [7]).

3) The 1940s–1960s: the period of expansion for synthetic fibers and filaments. John Rex Whinfield and his collaborator James Tennant Dickson obtained in 1941 polyester fibers in the form of polyethylene terephthalate [8].

Elastane (also known as Lycra® or spandex) was invented in 1959 by chemist Jr. Joseph Clois Shivers. It is a polyether-polyurea copolymer [9]. Initially called 'Fiber K', the trade name was later changed to 'Lycra®' [10].

**email: cornelia.mitran@incdtp.ro, elena.corneliaa@yahoo.com*

4) The 1960s – 1970s: the period of diversification of synthetic fibers. At this stage, due to the danger of extinction of artificial fibers, improvements in the manufacturing technologies of cellulosic fibers, especially short fibers, were made. Poly(paraphenylenediamine terephthalamide), also known as Kevlar®, was invented in 1964 by chemist Stephanie Kwolek and her team [11]. Richard B. Millington and Robert C. Nordberg developed in 1960 a technology to produce fibers with 99% carbon content, having as precursor artificial silk fibers (carbon fibers) [12].

Ethnographic textile artifacts are complex, both in terms of the polymeric materials that can be present in the composition of modern and contemporary textiles, as well as in terms of the techniques used to create them.

There are several collectibles that may pose a health hazard, although this hazard is not caused by the intervention of collectors or museum staff. An example of such health hazard are silk textiles, which may contain arsenic and lead that could have been added during the manufacturing process and may present a serious health hazard [13].

Additionally, there are also collectibles that were treated in the past with various pesticides, that have not been mentioned in any document [14], thereby endangering the health of museum staff and collectors. Objects that have already been treated with pesticides by collectors at the time of the purchase or collection and which were subsequently transferred to museums are often re-treated with chemicals by museum staff as a method of preventing pest infestation.

Biodegradation is a combination of 3 factors: an organism (harmful), a food source (textiles), and an appropriate environment. Generally, the organisms that are damaging to museum objects are humans, fungi, bacteria, insects, and rodents.

Textiles are mainly attacked by three types of pests: carpet beetles, clothing moths, stove fish (*Thermobia domestica*), and silver fish (*Lepisma saccharina*) [15]. Most of the damage to textiles is caused by carpet beetles and clothing moths.

One trend of modern analytical chemistry is the development of new analytical techniques and methods that can reliably identify and quantify components in complex samples, such as heritage samples. Due to the progressive use of many pesticides, this paper was focused on the detection and quantification of three pesticides: malathion, methoxychlor, and permethrin.

Determining organic pesticides can be problematic due to their characteristic volatility. Therefore, gas chromatography was the analytical method of choice for the present study.

Gas chromatography is one of the most widely used analytical techniques for characterizing volatile organic compounds that may be present in modern and contemporary art pieces [16-19].

## 2. Materials and methods

Abbreviations:
GC = Gas chromatograph
SIM = Selected ion monitoring
MS = Mass spectrometer

The first step in obtaining an appropriate analytical method has been the development of a SCAN method, process that has been previously described, in another work [20]. Because the detection limit and the quantification limit could not be reached using a scan method, a SIM method was optimized and validated in this paper.

A SIM method allows the mass spectrometer to detect specific compounds with high sensitivity. In SIM mode, the instrument is set to collect data at selected masses of interest, instead of scanning a wide range of masses.

SIM also allows the collection of several points on a chromatographic peak, thus increasing the accuracy and precision of the quantitative results.

The tests for optimizing the SIM method were performed on a standard solution containing the three pesticides of interest in ethyl acetate, at different concentration. The equipment used was an Agilent 6890N gas chromatograph with a mass spectrometer detector and Phenomenex ZB-5MSi column.

# 3. Results and discussions

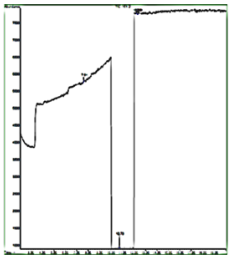
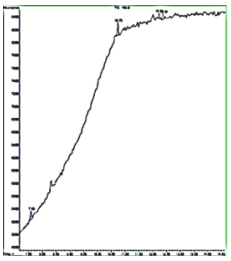
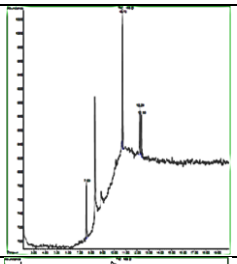
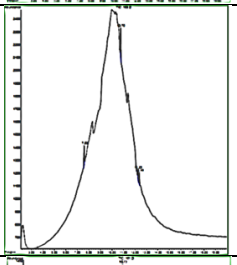
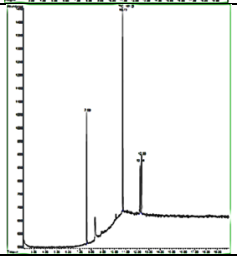
## 3.1. SIM method optimization

The optimization of the SIM method was performed by adjusting the MS parameters: selected ions and dwell. The GC parameters remained constant:

- injection volume: 1 µL, splitless mode
- T ºC inlet=300ºC
- flow = 1.2 mL/min, constant flow
- oven program: from 130ºC to 280ºC with 15ºC/min, hold 10 min at 280ºC
- TºC aux=300ºC

MS parameters and the results are presented in Table 1.

**Table 1.** SIM parameters and results

| Method | Selected ions | Dwell | 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<br>- 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<br>- 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 msec |  | The chromatographic peaks obtained for the concentration of 2 ppm 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<br>- methoxychlor: 113.60, 152, 152.10, 169, 169.10, 212, 212.10, 227, 227.10, 228<br>- permethrin: 44, 44.10, 163, 165, 183, 183.10, 184, 184.10, 207 | 50 msec |  | Because the idea of a SIM method is to have as few representative ions from a compound of interest as possible, fewer ions are still selected and the value of the dwell parameter is increased. This parameter is used to optimize the time cycle required to obtain 15-20 points or scans on a chromatographic peak. |
| Method 3 | - malathion: 93, 99, 125, 158, 173<br>- methoxychlor: 152, 212, 227, 227.10, 228<br>- permethrin: 163, 165, 183, 183.10, 184.10 | 100 msec |  | By decreasing the number of ions, the sensitivity of the method is increased, and the peaks obtained at 2 ppm concentration become much better defined and separated from the baseline. |
| Method 4 | - malathion: 93, 125, 127, 173<br>- methoxychlor: 152, 212, 227, 228<br>- permethrin: 163, 165, 183, 184 | 200 msec |  | The selected parameters are not adequate because the peaks are not well defined and separated from the baseline. |
| Method 5 | - malathion: 93, 125, 127, 173<br>- methoxychlor: 152, 212, 227, 228<br>- permethrin: 163, 165, 183, 184 | 50 msec |  | The resulting chromatogram shows that the peaks are separated from the baseline and well defined. |

The best results were obtained using method 5 because of well separated and defined peaks.

### 3.2. SIM method validation

To validate the previously optimized method, an 8-point calibration curve was performed at the following concentrations: 0.2 ppm, 0.5 ppm, 1 ppm, 1.5 ppm, 2 ppm, 3 ppm, 5 ppm, 10 ppm.

The validation parameters for the method are:

**1) Selectivity/ specificity**

Both selectivity and specificity are the performance parameters of the analytical method, which provide an overview of the robustness of the analytical method.

In the present paper, the selectivity has been demonstrated using the following approaches:

a)Overlapping the chromatogram corresponding to the solvent over the chromatogram of the standard mixture:

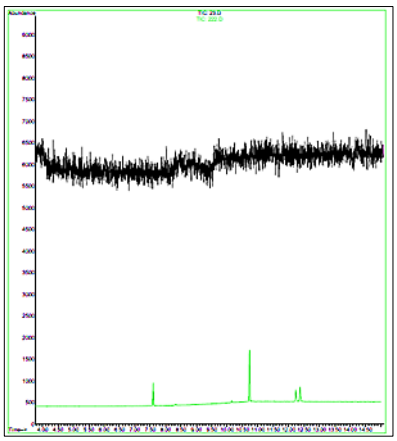


**Figure 1.** 3 ppm standard solution chromatogram overlay (green)/ solvent chromatogram (black)

The chromatogram corresponding to the standard solution of 3 ppm concentration (Figure 1) presents the 4 peaks corresponding to the analytes, while the chromatogram of the solvent only contains the baseline.

b) Selectivity assessment by determining the relative standard deviation (RSD%)

When selectivity is assessed in this manner, the RSD% must be less than 1%.

Procedure: RSD% was determined by injecting a standard solution of 3 ppm in 10 duplicates and evaluating the retention times that were obtained. The results are presented in Table 2.

**Table 2.** Selectivity assessed by RSD%

| Malathion | Methoxychlor | *cis*-Permethrin | *trans*-Permethrin |
|---|---|---|---|
| Retention time | | | |
| 7.596 | 10.730 | 12.234 | 12.370 |
| 7.596 | 10.730 | 12.234 | 12.370 |
| 7.597 | 10.730 | 12.234 | 12.370 |
| 7.596 | 10.730 | 12.235 | 12.370 |
| 7.596 | 10.730 | 12.234 | 12.380 |
| 7.596 | 10.730 | 12.234 | 12.370 |
| 7.595 | 10.730 | 12.234 | 12.370 |
| 7.596 | 10.729 | 12.233 | 12.370 |
| 7.596 | 10.730 | 12.234 | 12.370 |
| 7.596 | 10.730 | 12.234 | 12.370 |
| RSD% | | | |
| 0.04 | 0.03 | 0.04 | 0.30 |

The values of RSD% that were obtained after evaluating the retention times is less than 1% for all 4 analytes, demonstrating the selectivity of the method.

c) Determination of the chromatographic resolution between the components (Rs)

For a good separation, the resolution between two completely unseparated compounds must be at

least 1 - 1.5. In the case of completely separated compounds, the resolution is high.

**Table 3.** Chromatographic resolution between components

| | Retention time | Rs |
|---|---|---|
| Malathion | 7.60 | 21.58 |
| Methoxychlor | 10.73 | 8.80 |
| *cis*-Permethrin | 12.23 | 0.75 |
| *trans*-Permethrin | 12.37 | - |

The results presented in Table 3 demonstrate a good separation of the malathion analyte from methoxychlor and methoxychlor from cis-permethrin. Between the two isomers of permethrin, the chromatographic resolution obtained is less than 1, but corroborating the results obtained for the selectivity of the method using the other two evaluation methods, it is "admitted" that the method has selectivity for the three pesticides that were analyzed.

**2) Precision: in terms of repeatability and intermediate accuracy**

a) Repeatability

Repeatability expresses analytical variability under the same working conditions, for a short period of time, when the test is performed by a single operator, in a single laboratory, using a single analytical equipment and the same method [21].

The following parameters were determined:

- standard deviation of repeatability: Sr
- repeatability limit, with the formula: $r = 2.8 \times S_r$
- relative standard deviation of repeatability (%): $RSD_r = S_r \div X_m$

For chromatographic values, RSDr values (%) of maximum 20% are accepted, depending on the compound and the stability of the detector's response.

Procedure: 10 measurements of the pesticide mixture with a concentration of 3 ppm were performed during the same day, in the same laboratory, on the same equipment and method and by a single analyst (Table 4).

**Table 4.** $RSD_r$ results (%)

| | Malathion | Methoxychlor | *cis*-Permethrin | *trans*-Permethrin |
|---|---|---|---|---|
| Injection 1 | 4.30 | 3.80 | 4.00 | 4.00 |
| Injection 2 | 3.30 | 3.00 | 3.20 | 3.10 |
| Injection 3 | 2.80 | 2.80 | 3.20 | 2.90 |
| Injection 4 | 2.70 | 2.70 | 2.90 | 2.80 |
| Injection 5 | 2.70 | 2.50 | 2.90 | 2.80 |
| Injection 6 | 2.80 | 2.80 | 3.10 | 3.10 |
| Injection 7 | 2.90 | 2.60 | 3.30 | 3.00 |
| Injection 8 | 4.00 | 3.70 | 4.40 | 4.30 |
| Injection 9 | 3.90 | 3.50 | 4.00 | 3.90 |
| Injection 10 | 2.50 | 2.40 | 2.90 | 2.80 |
| $C_{mean}$, ppm | 3.19 | 2.98 | 3.39 | 3.27 |
| $S_r$ | 0.61 | 0.48 | 0.51 | 0.54 |
| R | 1.71 | 1.35 | 1.44 | 1.51 |
| $RSD_r$ | 0.19 | 0.16 | 0.15 | 0.17 |
| $RSD_r$, % | 19.19 | 16.15 | 15.18 | 16.53 |

b) Intermediate precision

In order to evaluate the intermediate precision of the method, the use of the Horwitz equation [22] and the Horwitz Report ($HorRat_r$) [23] is required. Using the Horwitz equation, the predicted relative standard deviation ($PRSD_R$) can be calculated.

$$RSD_r, \% = 2^{(1-0.5 \times logC)} \quad (1)$$

The value of $HorRat_r$ is the ratio between RSDr calculated from the laboratory data, to RSD provided from the Horwitz equation presented as $PRSD_R$, as follows:

$$HorRat_r = \frac{RSD_r}{PRSD_R} \quad (2)$$

For the evaluation of the parameter of interest, the accepted values range between 0.3 and 1.3.

Procedure: 10 different injections of the pesticide mix with a concentration of 3 ppm were performed for a period of 10 days, in the same laboratory, on the same equipment and method and by 4 different analysts (Table 5).

**Table 5.** Intermediate precision results

| | Malathion | Methoxychlor | *cis*-Permethrin | *trans*-Permethrin |
|---|---|---|---|---|
| Day 1 | 3.28 | 3.08 | 3.33 | 3.20 |
| Day 2 | 3.10 | 2.90 | 3.43 | 3.30 |
| Day 3 | 3.50 | 3.18 | 3.53 | 3.45 |
| Day 4 | 2.75 | 2.70 | 3.03 | 2.90 |
| Day 5 | 3.33 | 3.05 | 3.65 | 3.50 |
| Day 6 | 3.28 | 3.08 | 3.33 | 3.20 |
| Day 7 | 3.10 | 2.90 | 3.43 | 3.30 |
| Day 8 | 3.50 | 3.18 | 3.53 | 3.45 |
| Day 9 | 2.75 | 2.70 | 3.03 | 2.90 |
| Day 10 | 3.33 | 3.05 | 3.65 | 3.50 |
| $C_{mean}$, ppm | 3.19 | 2.98 | 3.39 | 3.27 |
| $S_r$ | 0.25 | 0.17 | 0.21 | 0.21 |
| R | 0.71 | 0.46 | 0.59 | 0.60 |
| $RSD_r$ | 0.08 | 0.06 | 0.06 | 0.07 |
| $RSD_r$, % | 7.97 | 5.55 | 6.25 | 6.53 |
| $HorRat_r$ | 0.05 | 0.03 | 0.04 | 0.04 |

**3) Detection limit (LD) and quantification limit (LC)**

Detection limit (LD) represents, according to ISO the "minimum detectable net concentration" or, according to IUPAC, the "minimum detectable value" [24].

The limit of quantification (LQ) is the lowest concentration or amount of analyte that can be determined quantitatively with an acceptable level of repeatability and accuracy.

Procedure for detection limit: 10 injections of a fortified blanc solution were performed at the lowest concentration (0.2 ppm). The detection limit was calculated according to the equation:

$$LD = 0 + 3 \times s_{sample} \quad (3)$$

where: s = standard deviation of the sample.

Procedure for quantification limit: 10 injections of a fortified blanc solution were performed at the lowest concentration (0.2 ppm). The limit of quantification was calculated according to the equation:

$$LQ = 0 + 10 \times s_{sample} \quad (4)$$

where: s = standard deviation of the sample.

**Table 6.** Results calculated for 0.2 ppm concentration

| | Malathion | Methoxychlor | *cis*-Permethrin | *trans*-Permethrin |
|---|---|---|---|---|
| LD | 0.06 | 0.05 | 0.04 | 0.06 |
| LQ | 0.18 | 0.17 | 0.14 | 0.20 |

The results obtained for the 0.2 ppm concentration are presented in Table 6. The values calculated for the detection limit are good for all analytes. The limit of quantification also has acceptable values, but the values of the limit of quantification in the case of *trans*-permethrin coincide with the lowest concentration in the calibration curve, therefore the two limits were calculated for the 0.5 ppm concentration. The results are presented in Table 7.

**Table 7.** Results calculated for 0.5 ppm concentration

| | Malathion | Methoxychlor | *cis*-Permethrin | *trans*-Permethrin |
|---|---|---|---|---|
| LD | 0.13 | 0.14 | 0.12 | 0.12 |
| LQ | 0.44 | 0.46 | 0.41 | 0.39 |

The results obtained for the 0.5 ppm concentration are better than those obtained in the case of the 0.2 ppm concentration, meaning that the calibration curve will be further performed at the following concentrations: 0.5 ppm, 1 ppm, 1.5 ppm, 2 ppm, 3 ppm, 5 ppm, 10 ppm.

**4) Working range and linearity**

The working range is the range of all concentrations in the calibration curve. In other words, it is the range between the lowest concentration and the highest concentration of the compound of interest, for which it is shown that the proposed protocol has adequate values of accuracy, precision, and linearity [25].

Procedure: standard solutions (multicomponent mixture) were injected in order to perform the calibration curve. Because the best values were obtained when calculating the quantification limit using the 0.5 ppm concentration as the first point of the calibration curve, the working range will be 0.5 to 10 ppm.

After plotting the calibration curve, the slope (sensitivity), the correlation coefficient, the residual standard deviation of the method, Sy, and the coefficient of variation of the method, CVx are calculated.

The correlation coefficient is automatically calculated by the software of the equipment once the calibration curve is plotted.

The answer is considered linear on the chosen concentration range if the value of the correlation coefficient is higher than 0.9900.

The coefficient of variation has values between 0 - 100%. If Cv = 0, there is no variation and all the values are equal to the average and to each other. If Cv → 0, the variation of the values is low, and the data obtained is homogeneous. Generally, it is admitted that the series has a high degree of homogeneity if Cv < 35%, and if Cv > 70-75%, it is stated that the variation is very large, and hides a heterogeneous structure of the community [26].

**Table 8.** Slope and correlation coefficient for each pesticide

| | Slope (sensitivity) | Correlation coefficient, r |
|---|---|---|
| Malathion | 81.00 | 0.9975 |
| Methoxychlor | 454.00 | 0.9985 |
| *cis*-Permethrin | 150.00 | 0.9980 |
| *trans*-Permethrin | 189.00 | 0.9965 |

The correlation coefficient is higher than 0.9900, indicating that the established working range is suitable for the proposed protocol.

**Table 9.** Results for the characteristic parameters of the method

| | 0.5 ppm | 1 ppm | 1.5 ppm | 2 ppm | 5 ppm | 10 ppm | $\bar{C}$ ppm | Sy | Sx | CVx (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Malathion | 0.47 | 1.03 | 1.24 | 1.65 | 2.50 | 4.40 | 9.35 | 2.69 | 0.03 | 1.12 |
| Methoxychlor | 0.48 | 0.90 | 1.21 | 1.61 | 2.37 | 4.24 | 9.18 | 2.64 | 0.01 | 0.20 |
| *cis*-Permethrin | 0.50 | 1.04 | 1.44 | 1.89 | 2.76 | 4.93 | 10.83 | 3.12 | 0.02 | 0.62 |
| *trans*-Permethrin | 0.49 | 1.02 | 1.36 | 1.82 | 2.64 | 4.76 | 10.89 | 3.15 | 0.02 | 0.51 |

The values of the CVx coefficient of variation (%) for the analytes of interest are low, meaning that the series has a high degree of homogeneity

**5) Accuracy**

The accuracy of an analytical procedure expresses the proximity between the value that is accepted as a value of reference and the value obtained analytically [27].

In the present paper, the following parameters were determined to assess the accuracy of the proposed protocol:

- Accuracy of measurements represents the ratio between the average of the results of all measurements of the standard solution of the same concentration and the true/ known value of that standard solution.

For chromatographic methods, the accuracy can vary between 75 - 125%.

- Rightness is a total systematic error and it is calculated as the difference between the average value of the analytical results and the accepted reference value. Rightness is expressed in terms of "bias".

- Method fidelity is calculated as a standard deviation of the results and it is interpreted as following: a higher standard deviation value reflects a lower method fidelity, while a lower standard deviation value reflects a higher method fidelity.

Procedure: 10 injections of the same standard solution of known concentration (3 ppm) were performed and the parameters described above were calculated (Table 10).

**Table 10.** Accuracy parameter results

| | Malathion | Methoxychlor | *cis*-Permethrin | *trans*-Permethrin |
|---|---|---|---|---|
| Average concentration (practical), ppm | 3.19 | 3.52 | 3.39 | 3.27 |
| Theoretical concentration, ppm | 3.00 | 3.00 | 3.00 | 3.00 |
| Fidelity (standard deviation, s) | 0.65 | 0.31 | 0.54 | 0.57 |
| Accuracy, % | 106.33 | 117.33 | 113.00 | 109.00 |
| Bias, % | 6.33 | 17.33 | 13.00 | 9.00 |
| Rightness, % | 83.54 | 83.20 | 93.25 | 83.97 |

As it can be seen in Table 10, the proposed method presents the appropriate accuracy for the quantification of the selected analytes.

## 4. Conclusions

The proposed method proved to be suitable for determining and quantifying the selected pesticides.

The method shows specificity and selectivity for the selected analytes. The detection limits ranged between 0.12 ppm and 0.14 ppm, while the quantification limits are below the lowest point in the calibration curve for all the selected pesticides. The correlation coefficient indicates a linear answer demonstrate a suitable working range. The result obtained for the accuracy shows a high method fidelity, and the appropriate accuracy for pesticide assessment. All the result obtained allow the use of this method for pesticides used in museums on textile materials.

The work will be continued with the optimization of an extraction method for the 3 pesticides that is suitable for textile materials that are part of modern and contemporary art objects.

**Acknowledgement:** This work was elaborated through Nucleu Program, conducted with MCI support, project no. 4N/2019/PN 19 17 05 01.

**References**

1. BORDEIANU D., (2013b), Capitolul II. Evolutia productiei de fibre textile, Curs Fibre Textile, p. 19.
2. Time life books, (1991), Inventive Genius (Library of Curious and Unusual Facts).
3. CROSS C.F., BEVAN E.J., (1892), Improvements in Dissolving Cellulose and Allied Compounds, British Patent no.8700.

4. CAROTHERS W.H., WILLIAMS I., COLLINS A.M., KIRBY J.E., (1937), Acetylene Polymers and their Derivatives. II. A New Synthetic Rubber: Chloroprene and its Polymers, Journal of the American Chemical Society, 53 (11), p. 4203.
5. SIVARAM S., (2017), Wallace Hume Carothers and the Birth of Rational Polymer Synthesis, Resonance, p. 339.
6. BAYER O., (1937), Classic PU Patent of the Month: Otto Bayer's Invention of Polyurethane and Polyurea, DE728981.
7. FINKENTSCHER H., HEUCK C., (1930), Verfahren zur Herstellung von Polymerisationprodukten, DE Patent 654989.
8. WHINFIELD J.R., DICKSON J.T., (1949), Improvements Relating to the Manufacture of Highly Polymeric Substances, Br. Patent 578 079; A Polymeric Linear Terephthalic Esters, U.S. Patent 2,465,319.
9. SHIVERS J.C., (1958), Segmented copolyetherester elastomers, U.S. Patent 3,023,192.
10. REISCH M., (1999), What's that stuff?, CENEAR 77(7), p. 70.
11. BROWN D.E., (2002), Inventing Modern America: From the Microwave to the Mouse, The MIT Press.
12. MILLINGTON R.B., NORDBERG R.C, (1961), Process for preparing carbon fibers, US Patent No. 3294489A.
13.***Conserve O Gram, Hazardous Materials in Your Collection, 1998, 2/10.
https://www.nps.gov/museum/publications/conserveogram/02-10.pdf
14. HAWKS, C., MAKOS, K., Inherent and Acquired Hazards in Museum Objects: Implications for Care and Use of Collections CRM., 2000, 5, 31-37.
http://www.jorgealiaga.com.ar/documentos/gestion-SG2-Depositos/Inherent%20Hazards%20in%20Museum%20Collections.pdf
15. ***Conserve O Gram, National Park Services. Identifying Museum Pest Damage, 2008, 1-7.
https://www.nps.gov/museum/publications/conserveogram/03-11.pdf
16. DOMENECH-CARBO, M.T., Novel analytical methods for characterizing binding media and protective coatings in artworks, *Anal. Chim. Acta*, 2008, 621, 109-139.
17. LA NASA, J., ZANABONI, M., ULDANCK, D., DEGANO, I., MODUGNO, F., KUTZKE, H., TOPALOVA-CASADIEGO, B., COLOMBINI, M.P., Novel application of liquid chromatography/mass spectrometry for the characterization of drying oils in art: elucidation on the composition of original paint materials used by Edvard Munch (1863– 1944), *Anal. Chim. Acta*, 2015, 896, 177-89.
18. IZZO, F.C., FERRIANI, B., VAN DEN BERG, K.J., VAN KEULEN, H., ZENDRI, E., 20th Century artists' oil paints: the case of the Olii by Lucio Fontana, *J. Cult. Herit*., 2014, 15, 557-63.
19. LLUVERAS-TENORIO, A., ANDREOTII, A., BONADUCE, I., BOULARAND, S., COTTE, M., ROQUE, J., Mass Spectrometric and Synchrotron Radiation based techniques for the identification and distribution of painting materials in samples from paints of Josep Maria Sert, *Chem. Cent. J*., 2014, 6, 45. DOI: 10.1186/1752-153X-6-45
20.MITRAN, E.C., SANDULACHE, I.M., SECAREANU, L.O., LITE, M.C., IORDACHE, O.G., PERDUM, E., RADU, G.L., Modern and contemporary textile museum collections: optimization method for pesticide analysis, *U.P.B. Sci. Bull. Series B*, 2020, 82 (3), 191-198.
https://www.scientificbulletin.upb.ro/SeriaB-Chimie_si_Stiinta_Materialelor.php?page=revistaonline&a=2&arh_an=2020&arh_ser=B&arh_nr=3
21.TANASE, I.Gh., PANA, A., RADU, G.L., BULEANDRA, M., Validarea metodelor analitice – Principii teoretice si studii de caz, Ed. Printech, 2007, 174.
22.HORWITZ, W., KAMPS, L.R., BOYER, K.W., *J. Assoc. Off. Chem*.,1980, 63, 1344. PMID: 7451398; https://pubmed.ncbi.nlm.nih.gov/7451398/
23.HORWITZ, W, ALBERT, R.J., The Horwitz Ratio (HorRat): A Useful Index of Method Performance with Respect to Precision, *Assoc. Off. Anal. Chem*., 2006, 89(4), 1095-1109. PMID: 16915851; https://pubmed.ncbi.nlm.nih.gov/16915851/

24.***Ghidul Eurachem: Adecvarea la scop a metodelor analitice - Un ghid de laborator pentru validarea metodelor și concepte legate de aceasta, LGC UK, 1998. http://www.eurachem.org/
25.ICH-Q2B, Guidance for Industry: Validation of analytical procedures; methodology, 1996. https://www.fda.gov/media/71725/download
26.DANCIULESCU, D., course"Statistică.Teorie și aplicații - Analiza seriilor de repartiție – Coeficientul de variație", 75. http://inf.ucv.ro/documents/danciulescu/curs4-curs-5-curs6.pdf
27.***European Pharmacopoeia 5.0, 2005, https://kampoeng2013.files.wordpress.com/2015/12/european-pharmacopoeia-5-with-all-supplements.pdf

Manuscript received: 26.05.2021