

## CYPERMETHRIN ASSESSMENT AND POSSIBLE PERSISTENCE IN GRAPES OR WINES

### EVALUAREA CIPERMETRINULUI DIN STRUGURI ȘI POSIBILA REMANENȚĂ LA VINURI

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**Abstract.** *The use of insecticides in crops is needed to provide an increase of production at relatively low cost. Lately increased chemisation to crop led to problems in the food, but also directly with animal health or in directly to human consumption. In the present work we propose to study such a substance, namely cypermethrin, which is used widely by human society. The method used is sensitive (SBSE-GC-MS) with a limit of ppb-level for identification and quantification relatively wide interval. We try to eliminate the intermediate steps in order to reduce other influences. Results showed the presence of these substances in grapes, but in relatively low concentrations and lack of it to wine, below the quantification limit of 1 ppb.*

**Key words:** cypermethrin, grapes, wines

**Rezumat.** *Folosirea insecticidelor în culturile de plante este o necesitate care asigură un spor de producție la costuri relativ scăzute. În ultima perioadă chimizarea accentuată a culturilor a dus la apariția de probleme atât cu produsul alimentar, dar și în mod direct cu sănătatea persoanelor sau animalelor consumatori direcți. Prin lucrearea de față ne propunem să studiem o astfel de substanță și anume cipermetrin care este folosit pe scară largă de către societatea umană. Metoda utilizată este sensibilă (SBSE-GC-MS) având o limită de identificare la nivel de ppb și de cantificare relativ largă. S-a încercat eliminarea pașilor intermediari astfel încât să nu mai existe contaminați de altă natură. Rezultate au arătat prezența acestei substanțe la struguri, dar în concentrații relativ mici și lipsa ei la vin sub limita de cuantificare de 1 ppb.*

**Cuvinte cheie:** cipermetrin, struguri, vin

## INTRODUCTION

Pyrethroids are a class of synthetically produced insecticides that are mainly used for domestic purposes to control insects such as mosquitoes. They behave very similarly to natural pyrethrins, which are derived from chrysanthemum flowers and are extremely toxic to fish and aquatic organisms, but have low toxicity towards humans. However, repeated exposure increases the risk of anaphylaxis and allergic

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reaction at very low concentrations and should be monitored.

Pesticides are substances or mixtures of substances intended for preventing, destroying, repelling or mitigating pests. A pesticide may be a chemical substance having antimicrobial or disinfectant properties, a biological agent (such as a virus or bacteria), or a device used against pests. Pests include insects, plant pathogens, weeds, molluscs, birds, mammals, fish, nematodes, and microbes that destroy property, spread disease, act as vectors for diseases or cause a nuisance. The word "pesticide" is an umbrella term for all insecticides, herbicides, fungicides, rodenticides, wood preservatives, garden chemicals and household disinfectants that may be used to kill some pests. Since pesticides varies in identity, physical and chemical properties, it's therefore logical to have them classified and their properties studied under their respective groups. Synthetic pesticides are classified based on various ways depending on the needs (Debbab *et. al.*, 2014).

Cypermethrin ( $C_{22}H_{19}Cl_2NO_3$ ) is a synthetic pyrethroid class of insecticide. It is commonly used to control various pests, including moth pests of cotton, fruit, and vegetable crops. It is also used for crack, crevice, and spot treatment to control insect pests in stores, warehouses, industrial buildings, houses and apartments, greenhouses, laboratories, ships, rail-cars, buses, trucks, and aircrafts. It may also be used in non-food areas in schools, nursing homes, hospitals, restaurants, hotels, and food processing plants (\*\*\*, 1989). Consumers expect a product to be free of pesticides (or low concentrations) and other contaminants (Thomas and Nagel, 2011).

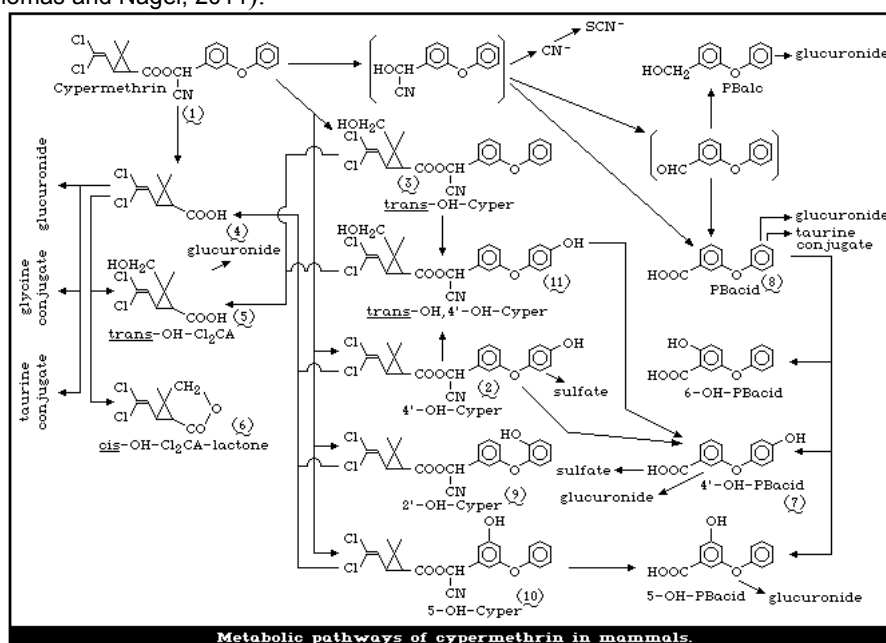


Fig. 1 - Metabolic pathways of cypermethrin in mammals (\*\*\*, internet)

It behaves as a fast-acting neurotoxin in insects. For mammals and this substance is broken in different metabolites (fig. 1) but mainly through 3-phenoxybenzoic acid with a LD50 about 200-300 mg/Kg.

Studies have been carried out on rats on the metabolism of the glucoside conjugate of 3-phenoxybenzoic acid, which occurs occasionally as a metabolite in plants. The results indicated that the rat hydrolyses the glucoside and then metabolizes the 3-phenoxybenzoic acid in virtually the same way as it would metabolize PBA liberated during the metabolism of cypermethrin.

## MATERIAL AND METHOD

Grapes samples and the wines are obtained through vinification by the traditional fermentation method for white wines technology. After gravity settler was done seeding with selected yeasts *Saccharomyces cerevisiae*. After alcoholic fermentation the samples of wine and the frozen grapes (at  $-18^{\circ}\text{C}$ ) were analysed. The samples studied from the following grape sort: Fetească albă; Fetească regală and Frâncușă harvested from Didactic Station "Vasile Adamachi" part of University of Agricultural Sciences and Veterinary Medicine "Ion Ionescu de la Brad" Iași.

For the analysis of the substance a gas chromatographic system is used that has a preconcentration unit SBSE (Stir Bar Sorptive Extraction). The system is an Agilent 7890B GC×GC (fig. 2) coupled to an ion trap mass spectrometer 420MS (ITMS) and also has the possibility to do ballistic GC to an electron capture detector ECD or to MS.

The Column Phenomenex WAX MS 30 m × 0.25 mm × 0.25 mm i.d. from Agilent 7890B GC oven. Injection is done in Split/Splitless inlet at splitless mode with a pulse pressure injection to 40 psi for 0.8 minutes. The injector purge flow of 100 mL/min for 0.75 minutes. The inlet temperature is  $250^{\circ}\text{C}$  and a constant flow mode 1 mL/min is maintained. Carrier gas used is Helium 6.0 purity.

The elution in the oven starts at  $80^{\circ}\text{C}$ ,  $15^{\circ}\text{C}/\text{min}$  to  $250^{\circ}\text{C}$  and then  $5^{\circ}\text{C}/\text{min}$  to  $300^{\circ}\text{C}$  and hold for 9 minutes. The total run time is 30 minutes.

The condition in the Agilent 240 Quadrupole Ion Trap MS are set to Auto-tune with +300 V to multiplier, and 45  $\mu\text{A}$  filament current. The acquisition is done with electron ionization (EI) and for better identification the MS<sup>3</sup> (MS/MS/MS) mode is used. The damping gas is 3.0 mL/min with a solvent delay for 17 minutes from the beginning. The source temperature is  $270^{\circ}\text{C}$ , the trap is set to  $150^{\circ}\text{C}$ , manifold to  $60^{\circ}\text{C}$  and the transfer line to  $300^{\circ}\text{C}$ .

For the ion extraction in the table 1 MS conditions are presented.

Table 1

The MS<sup>3</sup> ionization condition

Precursor	Excitation voltage	Product ion range	Emission current
MS1-181.3	2.2 V	151–153	45
MS2-152.2	3.4 V	74–124	45

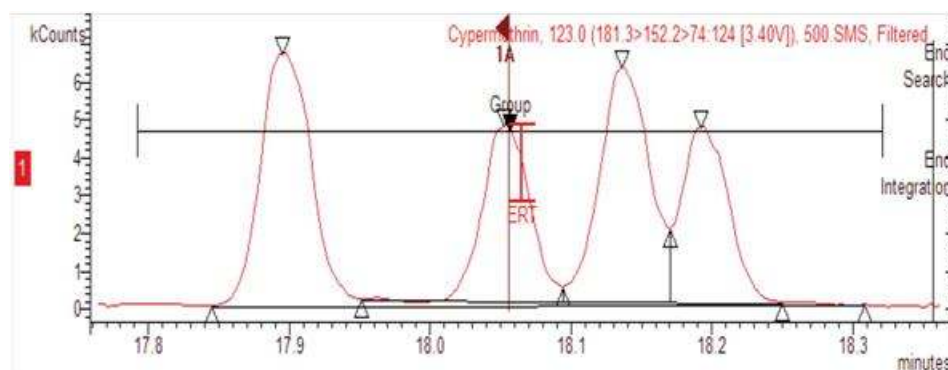
For the analysis the sample is directly placed in contact with the magnetic bar for adsorption of the compound of interest. The calibration of the instrument and the fine tuning was done by adding 5 ppm of 20% ethanoic solution to the magnetic bar and extraction for 60 minutes. The same procedure is done for spiking and recovery of the cypermethrin.



**Fig. 2 - SBSE-GC-ITMS**

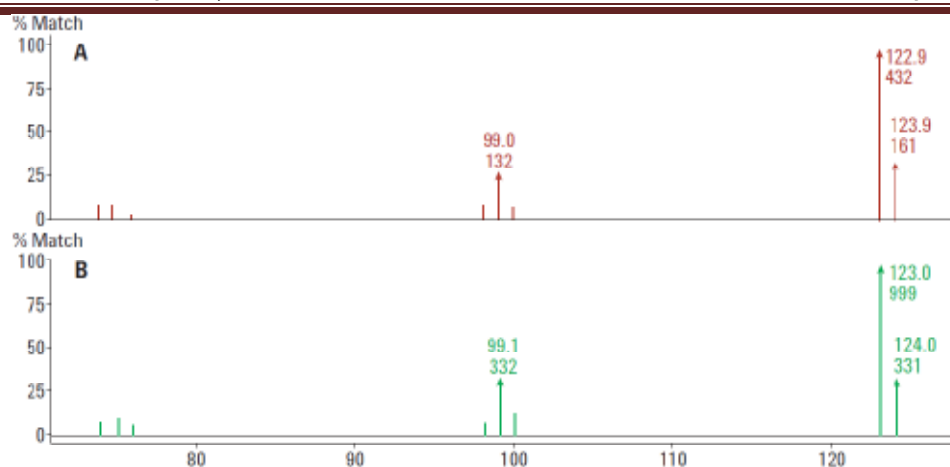
## RESULTS AND DISCUSSIONS

A series of five injection were made using the same methodology of extraction. Different concentration in triplicate were also injected and a range from 0.01-100 ppm. By using different specific transition a 10 ppb limit is detectible. As is presented in fig 3 there is a certain amount of interference close to the elution time of the substance, but the resolution between signals is better than 1.



**Fig. 3 - Cypermethrin specific pick of elution from a sample of must**

Corresponding to the standard injected in green (fig. 4) from the samples in red we have obtained a similarity that varies from 75-98% to the Nist 11 spectres database, but the spectral specific transition (fig. 3) are more specific then the deconvolution software.



**Fig. 4** - Cypermethrin specific pick of elution from a sample of must

The recovery rate is relatively good varying between 72.8 - 101.14 % for the test that we made.

Analysing the grapes observed that there is a quantity of pesticide to Feteascăregală ranged between 0.33 and 0.41 ppm. In the case of Feteascăalbă it was obtained 0.52 to 0.64. Somewhat higher values are in the case of grapes at Frâncușă 0.8 to 0.92. Low concentration determined do not certify that the grape vines were sprayed with this substance before harvest. A different story is the analysis of wine samples were the sample by MS<sup>3</sup> don't show this compound, so the limit that it's possible at 1 ppb it's not present in wine.

*Table 2*

**Results determine of oenological products**

Grape Variety	Grape ppm	Wine ppm
Fetească albă	0.58±0.06	< 0.001
Fetească regală	0.37±0.04	< 0.001
Frâncușă	0.86±0.06	< 0.001

The results are confirming once again that the wine is eliminates much of the reacting compound during the fermentation period.

## CONCLUSIONS

1. The analysis method for cypermethrin is efficient, convenient and can detect low concentrations of this insecticide.
2. This product residual wine is at ppb and not endanger the health of the consumer.
3. Low concentration determined do not certify that the grape vines were sprayed with this substance before harvest.

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