DETERMINATION OF AZOXYSTROBIN RESIDUES IN CUCUMBERS

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ABSTRACT

Systemic evalution of cucumber downy mildew disease intensity show that under the conditions of severe infection pressure and favorable ecological conditions for disease development, can be protected only by frequent and good quality fungicide application. The available literature data describe various conditions for determining the azoxystrobin residues. Mario Schirra *et al*. (2002) determined the level of azoxystrobine residues in grapefruit by gas chromatography with NPD detector, while Lenza - Rizos *et al*. (2005) dealt with the azoxystrobin residue from grapes to raisins, also by gas chromatography with ECD detector. In this paper, GLC-ECD and extraction with toluen and propa-2-ol, were evaluated to be applied in the analysis of azoxystrobin residues in cucumber. The extract was analysed by GLC with SPB 5 capillary column and ECD. The mean value, recovery for levels 0.02 - 1 mg/kg was 87.6%, with the relative standard deviation less than 10%. The metod showed linearity for all samples and linear correlation coefficient higher than 0.898. Under the optimized GLC-ECD conditions the retention time of azoxystrobin was 10.5 min, and LOD was 0.02 mg/kg. The results of the residue analysis show that in cucumber on our table the pesticide residues appear regularly, and they were under the MRL (1 mg/kg).

Key words: azoxystrobin, cucumber, food, pesticides, residue

IZVLEČEK

DOLOČEVANJE OSTANKOV (REZIDUOV) AZOKSISTROBINA V KUMARAH

Sistematična ugotavljanja stopnje okužb kumar od kumarne plesni (*Pseudoperonospora cubensis*) ob različnem infekcijskem pritisku in ekoloških razmerah, ki so ugodne za razvoj bolezni, so pokazala, da jo je mogoče zatreti z dobro in pogosto aplikacijo s fungicidi. V dostopni literaturi so opisane različne metode za določanje ostankov azoksistrobina. Mario Schirra *et al.* so določevali to substanco v grenivkah s plinsko kromatografijo z NPD detektorjem, medtem ko so Lenza-Rizos *et al.* (2005) ugotavljali ostanke iz grozdja vinske trte do smol s plinsko kromatografijo z detektorjem ECD. V tem prispevku bo prikazano določevanje azoksistrobina v kumarah z GLC-ECD in ekstrakcijo s toluenom in propan-2-olom. Ekstrakt so analizirali z GLC s kapilarno kolono SPB 5 in ECD. Srednja vrednost določitev za vsebnostne stopnje od 0,02 do 1 mg/kg je bila 87,6 %, z relativno standardno deviacijo manjšo kot 10 %.. Metoda kaže linearnost pri vseh vzorcih in linearni korelacijski koeficient, višji kot 0,898. V optimiziranih razmerah GLC-ECD je bil retencijski čas 10,5 min, LOD pa 0,02 mg/kg.

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Rezultati analize ostankov azoksistrobina v kumarah na poskusni njivi kažejo, da se ti pojavljajo redno in da so pod dovoljeno mejo (MRL) 1 mg/kg.

Ključne besede: azoksistrobin, kumare, živež, fitofarmacevtska sredstva, ostanki

1 INTRODUCTION

Downy mildew is the most important cucumber disease in Vojvodina. The first mass occurence and heavy yield losses in our conditions were registered during 1978. In our agroecological conditions the reason for poor chemical control efficiency, in spite of high fungicide efficiency lies in inadequate fungicide application in respect to application technique. Regarding the fact that the patogen infects the cucumber leaf from below through stomata to achieve application efficiency, it is essential to cover the leaf with fungicide.
The fungicide pre harvest interval (PHI) and pesticide residues are still the unsolved problems, especially in pikling cucumber type, because they are being picked every second or third day. In recent cucumber production and protection technology, these vegetable crops are the most risky regarding the pesticide residues and the production of healthy food.
Systematic evaluation of cucumber downy mildew disease intensity shows that in conditions of severe infection pressure and favorable ecological conditions for disease development, susceptible cucumber genotypes which are broadly used in Vojvodina can be protected only by frequent and good quality fungicide application. The results of residue analysis point that in cucumber on our table pesticide residues appear regularly.

2 MATERIALS AND METHODS

In recent years there has been growing interest in novel, broad spectrum fungicides currently designate »reduced risk« pesticides to humans, nontarget organisms, and environmental resources, with a diverse mechanism of action compared to other currently registered pesticides in a crop group. Among them, azoxystrobin, a systematic analog of the fungal metabolites of the strobilurins and oudemansins, has a very broad spectrum of activity and is effective against fungal pathogens belonging to the groups of *Oomycetes, Acaromycetes, Deuteromycetes,* and *Basidiomycetes* (Schirra *et al*., 2002). Figur 1. shows the chemical structure of azoxystrobin. Azoxystrobin was clasifield in the II group of poison materias.

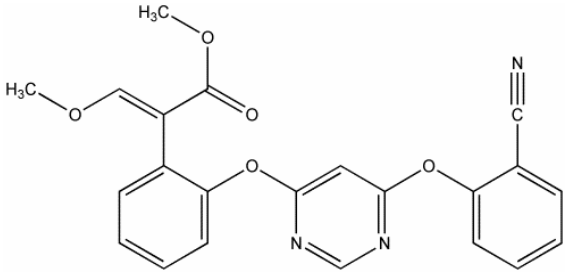

Figure 1: Molecural structure of azoxystrobin

Strobilurin fungicides (e. g. azoxystrobin) developed from naturally occurring products are used in many countries, because they have a broad spectrum of control against a large number of pathogens on various crops. These fungicides are not persistent in the environment, expected to be safe to nontarget species, and highly suitable for inclusion in

integrated pest management programs (Ishii *et al*.). MRL for azoxystrobin in cucumber in Serbia is 1 mg/kg (Mitić, 2004.), but in the world MRL for azoxystrobin is 0.05 mg/kg.
Cucumber was treated with Quadris in the concentration 1 l/ha. Samples for determination of azoxystrobin residues were collected immiediately after the treatment, after drying of deposit (day 0), after 2 days, 4 days, and after expiration of azoxystrobin PHI (7 days).
The optimization of determination method of the azoxystrobin residues from cucumber was done. Extraction and determination of the azoxystrobin residues from cucumber were made acoording the method Lenza-Rizos *et al*. (2005) and Giza *et al* (2003): 25 g homogenised sample was extracted with 50 ml toluene and 25 ml propan-2-ol. Propan-2-ol was removed by washing twice with 2 % Na_2SO_4 solution, and cleanup with mixture of celite and activated charcoal, followed by filtration. Extract was evaporated to 1 ml and analysed by gas chromatography with Hewlett Packard 5890 ser II, splitless injection mode, column: 30 m x 0.32 mm x 0.25 µm SPB 5 capilllary column and ECD. The injector temperature was operated at 230 °C, and the detector temperature at 300 °C. The column was held at 140 °C for 1 minute, rate 30 °C/min to 195° C and then 40 °C/min to 260 °C.

3 RESULTS AND DISCUSSION

Main recovery of azoxystrobin in cucumber, spiking levels from 0.02 to 1.0 mg/kg (0.02, 0.05, 0.1, 0.5 and 1.0 mg/kg) was 87.6 % with the relative standard deviation less than 10 %.

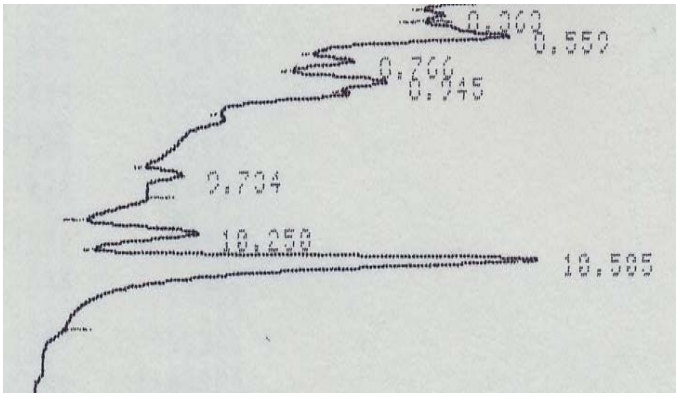

Figure 2: Chromatogram of cucumber sample with added azoxystrobin in concentration of 0.05 mg/kg

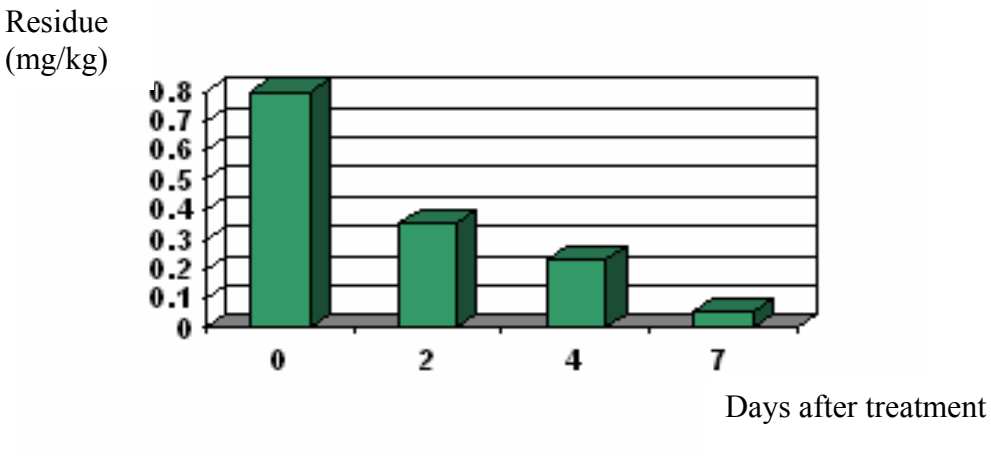

Figure 3: Azoxystrobin residue in cucumber

The metod showed linearity for all samples and linear correlation coefficient higher than 0.898. Under the optimized GLC - ECD conditions the retention time of azoxystrobin was 10.505 min (Fig. 2.). Limit of determination was 0.02 mg/kg and MRL for azoxystrobin in cucumber in Serbia and Montenegro is 1 mg/kg (Mitić, 2004.). Residues of azoxystrobin in cucumber samples collected 7 days after treatment were below the MRL.

4 CONCLUSION

The optimization of determination method of the azoxystrobin residues from cucumber was done. Extraction of the azoxystrobin residues from cucumber was made using the toluene/propan-2-ol mixture. Extract was evaporated to 1 ml and analysed by gas chromatography with SPB 5 capillary column and ECD. Main recovery of azoxystrobin in cucumber, spiking levels from 0.02 to 1.0 mg/kg was 87.6 % with the relative standard deviation less than 10 %. The metod showed linearity for all samples and linear correlation coefficient higher than 0.898.
The results of the residue analysis showed that in cucumber on our table the pesticide residues appeared regularly, and they were under the MRL (1 mg/kg).

5 REFERENCES

Giza, I., Sztwiertnia, U., 2003. Gas chromatographic determination of azoxystrobin and tefloxystrobin residues in apples, Acta Chromatographica, 13: 226-229.

Lentza-Rizos, Ch., Avramides, E. J., Kokkinaki, K., Residues of azoxystrobin from grapes to raisins, 2005. 4th MGPR International Symposium of pesticides in food and the environment in Mediterraniean countries and MGPR annual meeeting 2005, 72.

Ishii, H., Fraaije, B. A., Sugiyama, T., Noguchi, K., Nishimura, K., Takeda, T., Amano, T., Hollomon, D.W. 2001. Occurrence and molecular characterization of strobilurin resistance in cucumber powdery mildew and downy mildew, Phytopathology, 91: 1166-1171.

Mitić, V. N., 2004. Pesticidi u poljoprivredi i šumarstvu u Jugoslaviji 2002. Društvo za zaštitu bilja Srbije, Beograd.

Schirra, M., Cabras, P., Angioni, A., Brandolini, V., 2002. Residue Levels and Storage Decay Control in Cv. Star Ruby Grapefruit after Dip Treatments with Azoxystrobin, Journal of Agricultural and Food Chemistry, 50: 1461-1464.