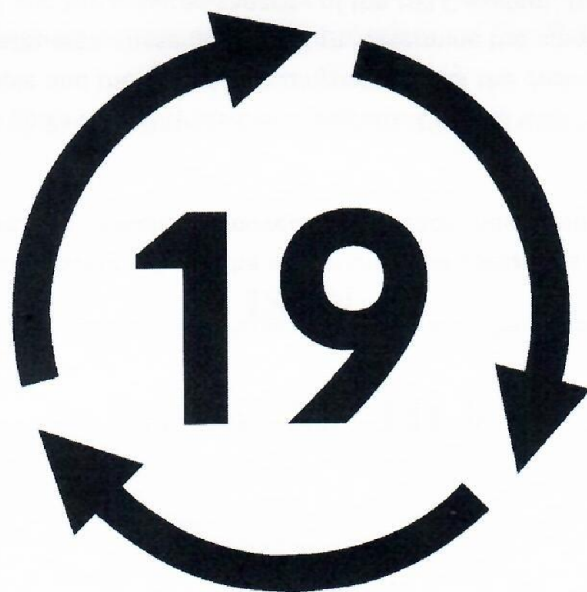


PROCEEDINGS OF  
**THE 19<sup>th</sup> INTERNATIONAL SYMPOSIUM ON  
ANALYTICAL AND ENVIRONMENTAL PROBLEMS**

23 September 2013

Edited by  
**Zoltán Galbács**



**SZAB**  
**SZEGED, HUNGARY**

**THE 19<sup>th</sup> INTERNATIONAL SYMPOSIUM ON ANALYTICAL AND  
ENVIRONMENTAL  
PROBLEMS**

***Organised by***

**SZAB Kémiai Szakbizottság Analitikai és Környezetvédelmi  
Munkabizottsága**

**Scientific Committee**

Prof. Dr. **RUDOLF KASTORI** *academician, Chairman* (Novi Sad, Serbia)

Dr. Zoltán Galbács, *Secretary* (Szeged, Hungary)

Prof. Dr. Etelka Tombácz (Szeged, Hungary)

Dr. Gábor Galbács (Szeged, Hungary)

Prof. Dr. Zeno Garban corresponding member of the Romanian Academy  
(Timisoara, Romania)

Prof. Dr. Petru Negrea (Timisoara, Romania)

**ISBN**

**978-963-315-141-9**

***Sponsors***

**Gábor Galbács, Béla Gyuresik, Attila Jancsó  
SZAB**

- Katalin Slezák, Ákos Doktor, Ferenc Orosz, Aleš Jezdinský : EFFECT OF SAMPLING DATE ON SOME INSIDE VALUE OF NANTES TYPE CARROT ROOTS (Page 217; File: W217-220)
- Máté Mihály, Kitti Nagy, Katalin Slezák : EFFECT OF POTASSIUM CHLORIDE ON THE YIELD AND FRUIT QUALITY OF SWEET PEPPER IN INTENSIVE OPEN-FIELD CULTIVATION (Page 148; File: W148-151)
- Kitti Sárközi, Judit Krisch, András Papp : EFFECT OF GREEN TEA ON ARSENIC TOXICITY IN RATS (Page 261; File W261-264)
- Adrian Laza, Georgeta Pop: STUDY REGARDING FLAX PHYTOREMEDIATION ABILITY (Page 257; File W257-260)
- N. Czirbus, T. Nyilas, L. Bíró, G. Bozsó, K. Kiss, M. Hetényi: THE ORIGIN OF HEAVY METAL CONTENT IN SOILS OF AGTELEK KARST (Page 52; File W52-55)
- Sanja Lazic, Dragana Sunjka, Nada Grahovac, Varéria Guzsvány: STABILITY TEST OF BENTAZON, DICAMBA AND 2,4-D IN WATER (Page 297; File W297-300)
- Sanja Lazic, Dragana Sunjka, Nada Grahovac, Valéria Guzsvány: DETERMINATION OF ACETAMIPRID IN SWEET CHERRY SAMPLES (Page 56; File W56-59)
- Pelea George Narcis, Costescu Ioana Alina, Man Teodor Eugen: ENVIRONMENTAL IMPACT OF IRRIGATION AND LAND IMPROVEMENT WORKS IN BIRDA LOCALITY, TIMIȘ COUNTY, ROMANIA (Page 237; File W237-240)
- Silvica Oncia, Loredana Copăcean, Mihai Herbei : GIS TECHNIQUE IN REPRESENTING EDAPHIC ENVIRONMENTAL QUALITY OF THE ADMINISTRATIVE TERRITORY OF DUMBRAVA (Page 152; File W152-155)
- Tünde Nyilas, Gábor Nagy, Márton Papp and Mariann Imre: THE EFFECTS OF CULTIVATED AGRICULTURAL FIELDS ON THE WATER- AND SOIL CHEMISTRY OF THE LAKE NAGYSZÉKSÓS (HUNGARY) (Page 99; File W99-102)
- Puskás Irén, Farsang Andrea, Bartus Máté: A VÁROSI, KÖZTÉRI TALAJOK KÖRNYEZETI PUFFERKAPACITÁSÁT MEGHATÁROZÓ PARAMÉTEREK ÉRTÉKELÉSE BUDAPEST, SZEGED PÉLDÁJÁN (Page 44; File W44-47)
- Suciu (căs.Bigyilan) Laura, Șumălan Radu, Viliga Lucian Florin: ENVIRONMENTAL IMPACT ANALYSIS ON PLANTS USING INTEGRATED SENSOR SYSTEM (Page 313; File W313-316)
- Viliga Lucian Florin, Șumălan Radu, Suciu (căs.Bigyilan) Laura: STUDIES REGARDING WATER STRESS TOLERANCE ON SOME SORGHUM GENITYPES (Page 119; File W119-122)

## DETERMINATION OF ACETAMIPRID RESIDUES IN SWEET CHERRY SAMPLES

Lazić Sanja, Šunjka Dragana, Grahovac Nada, Guzsvány Valéria

Faculty of Agriculture, University of Novi Sad, Trg Dositeja Obradovića 8, Novi Sad, Serbia  
 Institute of field and vegetable crops, Maksima Gorkog 30, Novi Sad, Serbia  
 Faculty of Science, University of Novi Sad, Trg Dositeja Obradovića 3, Novi Sad, Serbia  
 e-mail: [DRAGANAS@POLJ.UNS.AC.RS](mailto:DRAGANAS@POLJ.UNS.AC.RS)

### ABSTRACT

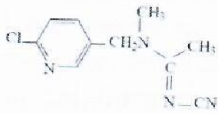
In this paper we have developed an analytical method for the fast determination of acetamiprid residue in sweet cherry samples. The experiment was carried out using blank sample spiked with a solution of acetamiprid insecticide at three levels. This analyte was extracted with acetonitrile from fortified sweet cherry samples using QuEChERS sample preparation procedure. Insecticide determination and quantification were performed by HPLC/DAD using reversed phase procedure utilized an Agilent Zorbax C<sub>18</sub> cartridge (50 mm × 4.6 mm internal diameter, 1.8 μm particle size). Mobile phase was acetonitrile/1.5% CH<sub>3</sub>COOH solution. Acetamiprid showed linear calibrations from 0.05–2.5 μg/ml with correlation coefficients of 0.995%. Limit of quantification (LOQ) were established as 0.014 mg/kg. Precision values expressed as relative standard deviation of the retention times and of the peak areas were 0.16 and 1.29%, respectively. Recoveries of the acetamiprid were in the ranged 80-94%. The proposed method is rapid, simple and could be utilized for the routine analysis of acetamiprid residues in sweet cherry samples.

### INTRODUCTION

Fresh fruits are the important part of a healthy diet because of the presence of significant amount of nutrients and minerals in them. At the same time, they can also turn out to be source of toxic substances such as pesticides. Pesticide residues can be found even when they are applied in accordance with good agricultural practices.

In order to reduce the use of organophosphates in protecting cherries, recommended for use an alternative compounds, such as those from the class of neonicotinoids. Over the past 15 years neonicotinoids have gained increasing interest in the agricultural sector across Europe (Council Directive 91/414/EEC). These insecticides are the fastest growing class of insecticides introduced to the market since the launch of the pyrethroids (Muccio et al., 2006).

Table 1. Physico-chemical properties of acetamiprid

Common name/ molecular formula/CAS No.	Chemical name (IUPAC)	Structural formula
Acetamiprid C <sub>10</sub> H <sub>11</sub> ClN <sub>4</sub> (160430-64-8)	(E)-N1-[(6-chloro-3-pyridyl)methyl]- N2-cyano-N1- Methylacetamide	

Acetamiprid is a systemic neonicotinoid insecticide for foliar and soil application (table 1). Besides its positive effects, acetamiprid also has been posing various health risks to consumers. Due to the growing use of insecticides from the family of neonicotinoids, their increased presence in the environment is evident. For this reason, the concentration of acetamiprid residues in agricultural products, especially in fruit for using in fresh form should be monitored. The determination of low concentrations of this pesticide in matrices, such as fruits, requires the application of an effective extraction, followed by a final chromatographic determination in order to separate as much as possible the analyte from the matrix interference substance. Moreover, there is a some alternative analytical approaches to the conventional methods of pesticides determination (Guzsvány et al., 2012, 2012a).

In this paper we have developed an analytical method for the fast determination of acetamiprid residue in sweet cherry samples. Acetamiprid was extracted from sweet cherry samples using QuEChERS sample preparation procedure, while insecticide determination and quantification were performed by HPLC/DAD.

## **MATERIALS and METHODS**

### **Chemicals and solutions**

Acetamiprid (purity 98.1%) was purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany). Acetonitrile (HPLC grade) and CH<sub>3</sub>COOH were obtained from J.T. Baker (Germany). QuEChERS dispersive SP extraction and clean-up kits were from Agilent, USA. A stock solution of acetamiprid was prepared in acetonitrile at a concentration of 100 µg/ml. Fortification levels and working calibration solutions for HPLC analysis were prepared via further dilution with acetonitrile, achieving concentrations in a range from 0.05 to 2.5 µg/ml. Fortified and calibrated standard solutions were stored in a refrigerator (4 °C).

### **Analytical procedure**

Extraction of acetamiprid from sweet cherry samples performed using QuEChERS-based method. Insecticide determination and quantification were performed by HPLC with diode-array detection (Agilent 1100, United States) using reversed phase procedure utilized an Agilent Zorbax C<sub>18</sub> cartridge (50 mm × 4.6 mm internal diameter, 1.8 µm particle size). Mobile phase was acetonitrile/1.5% CH<sub>3</sub>COOH solution (30/70). The column temperature was 25 °C, with a flow rate 1 ml/min. Injected volume was 2.5 µl. The detection wavelength was set to 254 nm.

### **Validation of the analytical method**

Method validation was performed in accordance with Document SANCO/12495/2011. Fortified samples were prepared by spiking 10 g of sweet cherry, previously homogenized, with the appropriate volumes of working standard acetamiprid solutions ranged from 0.75-2.25 µg/ml.

## **RESULTS**

HPLC/DAD chromatogram of acetamiprid standard in acetonitrile concentration of 0.75 µg/ml and in matrix-matched sample with 0.75 µg/ml acetamiprid are shown in figure 1. Using the selected conditions the linearity of the calibration curve was evaluated at a concentration range between 0.05–2.5 µg/ml using nine calibration solutions prepared in acetonitrile. Calculations were done using the peak areas and linear regression was used for

quantification and calibration curve. The calibration curves were linear with correlation coefficients of 0.995 (figure 2). The analytical parameters for method determination of acetamiprid in sweet cherry samples are presented in table 2.

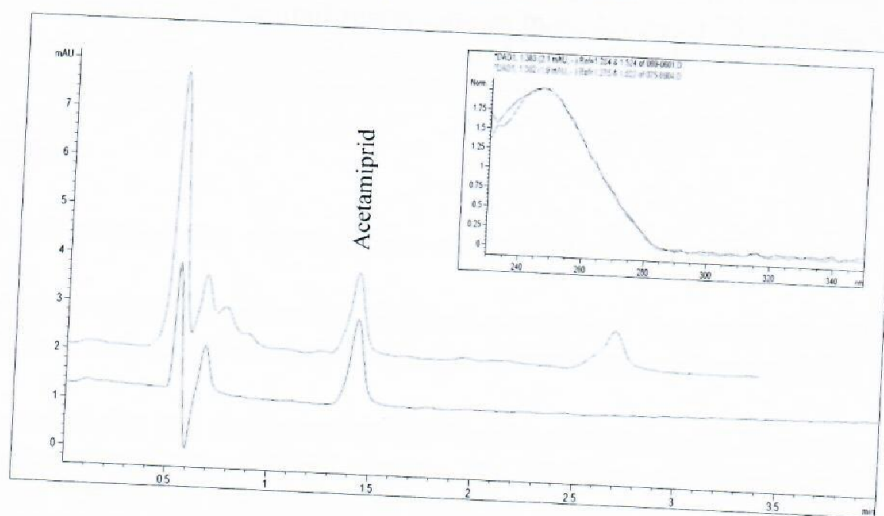


Figure 1. HPLC chromatograms of acetamiprid standard (blue) and spiked sweet cherry (red) at a concentration of 0.75 µg/ml, with UV apex spectrum of acetamiprid in ACN and matrix

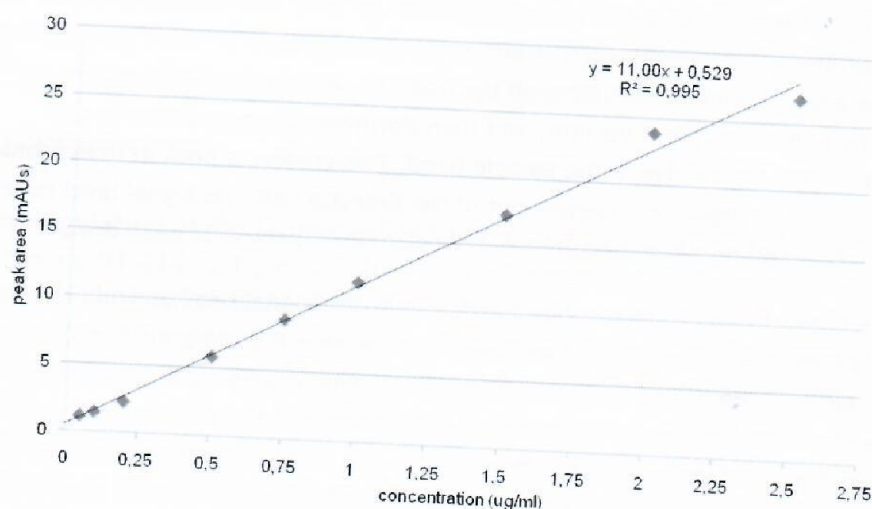


Figure 2. Calibration curve for acetamiprid standard in acetonitrile

Table 2. Analytical parameters for HPLC/DAD determination of acetamiprid

Parameter	Concentration interval (µg/ml)	Slope <sup>a</sup>	Correlation coefficient <sup>a</sup>	LOQ (mg/kg)
Acetamiprid	0.05-2.5	11.00x	0.995	0.014

<sup>a</sup> $Y = ax + b$

Limit of quantification (LOQ) for acetamiprid was estimated from the fortified samples. LOQ were established as 0.014 mg/kg. Precision value was expressed as relative standard deviation (RSD). The retention time of acetamiprid was 1.384 min. The repeatability of the retention

times and peak areas were checked by injecting the standard solution of acetamiprid (0.75 µg/ml) five times. Relative standard deviations (*RSD*) of the retention times and of the peak areas were 0.16 and 1.29%, respectively. The recovery was carried out using blank sample spiked with a solution of acetamiprid insecticide at three levels (0.75-2.25 mg/kg). The mean recoveries were in the range of 80-94% at these three spiking levels with associated relative standard deviations (*RSDs*) in the range of 1.08-2.55%.

## CONCLUSIONS

- In this work method for determination of acetamiprid in sweet cherry samples was developed.
- Considering the obtained values of analytical parameters, the proposed method proved to be an efficient and sensitive method for the determination of acetamiprid in samples of cherries.
- Having in mind that the maximum residue levels of acetamiprid in sweet cherries is 0.2 mg/kg (Serbian legislation; Official Gazette, No. 25/2010) and 1.5 mg/kg (EU legislation; Reg. EU No 212/2013), the method is sensitive enough for the determination of these pesticide at concentrations well below permissible levels.
- Hence, the method may find further application in the analysis of real sweet cherry samples contaminated with these insecticides at a ppb level.

ACKNOWLEDGEMENT. This research is a part of project funded by the Ministry of Education and Science of the Republic of Serbia, Grant No. TR31038.

## LIST OF REFERENCES

- Commission Regulation of the European Parliament and Council (EU) No 212/2013.  
Council Directive 91/414/EEC, of 15 July 1991 concerning the placing of plant protection products on the market (OJ L 230, 19.8.1991, p. 1).  
Directorate of General Health and Consumer Protection Document No. SANCO/12495/2011, Method validation and quality control procedures for pesticide residues analysis in food and feed.
- Guzsvány V., Lazić S., Vidaković N., Papp Zs. (2012) Derivative spectrophotometric determination of acetamiprid in the presence of 6-chloronicotinic acid. *Journal of Serbian Chemical Society*. 77(0), p. 1-11.
- Guzsvany V., Rajić Lj., Jović B., Orčić D., Csanadi J., Lazić S., Abramović B. (2012a) Spectroscopic monitoring of photocatalytic degradation of the insecticide acetamiprid and its degradation product 6-chloronicotinic acid on TiO<sub>2</sub> catalyst. *Journal of Environmental science and health part A-toxic/hazardous substances&environmental engineering*. 47(12), p. 1919-1929.
- Muccio A.D., Fidente P., Barbini D.A., Dommarco R., Seccia S., Morrica P. (2006) Application of solid-phase extraction and liquid chromatography– mass spectrometry to the determination of neonicotinoid pesticide residues in fruit and vegetables. *Journal of Chromatography A*. 1108, p. 1–6.
- Official Gazette of the Republic of Serbia, No. 25/2010 and 28/2011.