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**Vojislava BURSIĆ, Gorica VUKOVIĆ, Bojana ŠPIROVIĆ, Sanja LAZIĆ, Mira PUCAREVIĆ, Tijana ZEREMSKI [1]**

# QuEChERS METHOD FOR DETERMINATION OF PESTICIDE RESIDUES IN CHERRIES

## SUMMARY

A simple multiresidue method was evaluated for the determination of pesticide residues in cherries using GC-MS/MS for the analysis. A modified QuEChERS method was evaluated in the coloured matrix, such as cherries. This extraction method involves sample extraction with acetonitrile for 3 min on vortex mixer and permits the salt-out liquid−liquid partitioning step using magnesium sulfate anhydrous, sodium chloride, trisodium citrate dihydrate and sodium citrate dibasic sesquihydrate. After shaking and centrifugation, the cleanup was done by adding 5 ml of extract to anhydrous $MgSO_4$, PSA, and carbo activatus. After a repeated centrifugation the 2 ml of extract was evaporated to dryness, and reconstituted in 2 ml of acetone. The optimized analytical conditions were evaluated in terms of recoveries, reproducibility, limits of detection, and matrix effects for 17 pesticides. Some significant matrix effects observed for most of the tested pesticides were eliminated using matrix-matched calibration. The linearity was studied in the range of 0.05–1.0 μg/ml with the $R^2$ higher than 0.99. The recovery data were obtained by spiking blank samples at three concentration levels (0.05, 0.1 and 0.5 mg/kg) yealding recoveries in the range of 77.5–102.4%. The precision values were lower than 11.14% for the intraday precision. The LOQs were established as 10 μg/kg.

**Keywords:** QuEChERS, pesticide residues, cherries, GC-MS/MS.

## INTRODUCTION

Fruit production in Serbia is economically significant due to favourable climatic and soil conditions for growing a great number of fruit species with cherries and sour cherries being most promionent. (Sredojević, 2011). Cheerry production, besides by agents of plant diseases , phytopatogenic bacteria and viruses (*Blumeriella jaapii*, *Monilina spp*., *Stigmina carpophila*), can also be badly affected by pests *Rhagoletis cerasi* (cherry fruit fly), *Myzus cerasi* (cherry blackfly), *Aculus fockeui* (sour cherry rust mite) and *Rynchites auratus* (sour cherry weevil) (Miletić and Tamaš, 2011). In order to obtain a competative

[1] Vojislava Bursić (author for correspondence: bursicv@polj.uns.ac.rs), Sanja Lazić, Faculty of Agriculture, University of Novi Sad, Serbia; Gorica Vuković, Institute of Public Health of Belgrade, Belgrade, Serbia; Bojana Špirović, Faculty of Agriculture, University of Belgrade, Serbia; Mira Pucarević, Educons University, Faculty for Environmental Governance and Corporate Responsibility, Sremska Kamenica, Serbia; Tijana Zeremski, Institute of Field and Vegetable Crops, Novi Sad, Serbia.

product for the market it is necessary to apply a great many treatments of the fruits aimed at the control of diseases and pests. On our market there are 46 compounds registered for the use in cherry protection out of which 19 are insecticides, 5 acaricides and 22 fungicides (Sekulić and Jeličić, 2011). Since cherry fruit is predominantly used as fresh food and to a lesser extent in food processing there is a justified concern that, due to a great number of treatments, cherry fruit can contain pesticide residues above the maximum residue levels – MRLs (Bursić et al., 2011).

During the development of agricultural production pesticides have become an important tool in plant protection as a support to food production.The currant procedures in agricultural production imply a widespread application of pesticides and fertilizers. On the market of the European Union there are more than 1100 pesticides currently registered by the EU Document No. 3010. The frequent use of these substances turned pesticides from „friends“ into a very dagerous threat to human health (Rekha et al., 2006). These components are found in food in traces and have a negative effect if their content exceeds the maximum residue level. Health safety of the food is of a particular importance to consumers, food industry and economy (Jevšnik et al., 2008). The pesticide residues above the maximum residue levels in agricultural products and food (MRL), in fruit and vegetables, meat, fish, milk and dairy products are the result of their inadequate application in agricultural practice and storage.

Owing to the appllication of analitical methods which have made the identification and determination of pesticide residues possible we have become aware of the dangers which they pose. Pesticides comprise a very heterogenous group of chemical compounds with various biological, chemical and physical properties and that is why there is no unique method or technique for their determination. At present there are various analytical methods for pesticide analysis with gas and liquid chromatography as predominant. The most appropriate method for the determination of pesticide residues in food is the application of chromatographic methods with different procedures of sample preparation (Torres et al., 1996; Schenck et al., 2004) Anastassiades et al., 2003). For a number of years the sample preparation received less attention than chromatographic separation and detection methods (Smith, 2003). The most efficient approach to pesticide analysis is the use of multiresidual methods (MRM). He first recorded MRM method was introduced in 1960 for the determination of non-polar organocholoride pesticides in non-fat food (Mills et al., 1963). Mills`s method is based on the extraction by acetonitrile, extract dilution with water and pesticide re-extraction in non-polar solvent. The subsequent research work was directed towards broadening the polarity range so as to cover a greater number of pesticides of various polarity just by one determination. The application of new solvents at the early stage of extraction as well as the addition of sodium chloride (Becker et al., 1971; Luke et al., 1975; Specht et al., 1980) were studied aimed at the recovery increase of more polar analytes.

The growing concern over the environmental protection led to the decrease in the application of toxic solvents and development of extraction method on solid phase (SPE) (Casanova, 1996) in order to avoid liquid-liquid extraction (LLP) as a purification procedure.The further decrease in solvent application as well as in sample preparation time resulted in the development of a number of alternative extraaction procedures: matrax solid phase dispersion (MSPD), supercritical fluid extraction (SFE), solid phase microexstraction (SPME). Anastasiades et al. (2003) developed a quick, essential, cheap, efficient, robust and safe method (QuEChERS) so as to overcome the limitations of the existing preparation methods.

The trends in recent years have been directed towards the decrease in sample amounts for the analysis with the approach which is safe and less harmful to the environment and at the same time implies a quicker, simpler method for sample preparation with simultaneously providing high recovery and good precision (Bursić et al., 2012). The QuEChERS method uses acetonitrile, with the application of adequate combination of salts, dinatrijum hidrogen citrata seskvihidrata, water-free magnesium sulfate and sodium chloride with the purification procedure by primary-secondary amine (PSA) with the addition of water-free magnesion sulfate which results in a better separation of phases without dilution. In the purification of cherry extracts the active charcoal is used which has a strong affinity to planar molecules thus efficiently eliminating the the pigments from the extrct (Vuković et al., 2012).

The paper deals with the QuEChERS method for the determination of the residues of dodina, hlorpirifosa, bupirimata, fenarimola, flutriafola, flusilazola, penkonazola, krezoksim-metila, ditianona, dimetoata, difenokonazola, hlorotalonila, pirimetanila, azinfos-metila, kaptana, cipermetrina, boskalida and trifloksistrobina in cherries. PCB 52 is used as an internal standard. Cherries are rather demanding as a matrix in which the pesticide residues are determined due to the present pigments. Therefore, active charcoal is added in the analysis as it has a strong affinity towards planar molecules thus causing discolouration of the extract.The extract obtained in this way was analysed by gas chromatography with the quadropole mass spectometry– GC-MS/MS.

## MATERIAL AND METHODS

**Chemicals and apparatus** The analitical standards manifactured by Dr. Ehrenstorfer GmbH, Germany which were used in the research work are fenoxycarb (99.3%), chlorphyrifos (99.5%), bupirimate (99.5%), fenarimol (99.0%), flutriafol (95.8%), flusilazol (99.5%), penconazole (99.7%), krezoxim-methyl (99.7%), dithianon (98.6%), dimethoate (98.0%), dinocap (99.0%), chlorothalonil (97,5%), pyrimethanil (97.5%), azinphos-methyl (99.0%), captan (98.8%), cypermetrin (95.8%), boscalid (99.0%) and trifloxystrobin (99.9%). As an internal standard PCB 52 (Fluka>99%) was used in the concentration of 1 mg/ml of the basic standard in toluol with the dilution in acetonitrile up to 1.0 μg/ml. The basic standard solutions were prepared by dissolving an analytical

standard in acetone while the working solution i.e. the mixture of the studied pesticides was obtained by mixing and diluting the basic standards with acetone resulting in the final mass concentration of 10 μg/ml. The QuEChERS extraction comprised sodium chloride (J.T. Baker, Holland), trisodium citrate dihydrate (Zorka pharma, Šabac, Srbija), anhydrous magnesium sulfate(Hemrad, Belgrade, Serbia), disodium hydrogen citrate sesquihydrate (Sigma–Aldrich, Germany), bondesil-PSA (Agilent technologies, USA), active charcoal, acetone and acetonitrile (J.T. Baker, Holland).

The gas chromatograph Agilent 7890 GC (Agilent Technologies) was used in the researsch work. The detector was Agilent 7000B with triple quadropole mass spectometer. The ionization was carried out by elecron impact (EI) with the energy of 70 eV.

Table 1. Chemical characteristics of the studied pesticides

| Pesticides | Chemical group | Molecular weight | Molecular formula | MRL (mg/kg) |
|---|---|---|---|---|
| Acetamiprid | Neonicotinoid | 222.68 | $C_{10}H_{11}ClN_4$ | 0.20 |
| Azinphos-methyl | Organophosphate | 317.30 | $C_{10}H_{12}N_3O_3PS_2$ | 0.50 |
| Boscalid | Carboxamide | 343.21 | $C_{18}H_{12}Cl_2N_2O$ | 3.00 |
| Bupirimate | Pyrimidine | 316.42 | $C_{13}H_{24}N_4O_3S$ | 0.05 |
| Cypermethrin | Pyrethroid | 416.32 | $C_{22}H_{19}Cl_2NO_3$ | 1.00 |
| Difenoconazol | Triazole | 406.30 | $C_{19}H_{17}Cl_2N_3O_3$ | 0.30 |
| Dimethoate | Organophosphate | 229.28 | $C_5H_{12}NO_3PS_2$ | 0.20 |
| Dinocap | Dinitrophenol | 364.18 | $C_{18}H_{24}N_2O_6$ | 0.05 |
| Dithianon | Quinone | 296.32 | $C_{14}H_4N_2O_2S_2$ | 2.00 |
| Fenarimol | Pyrimidinyl | 331.20 | $C_{17}H_{12}Cl_2N_2O$ | 1.00 |
| Fenoxycarb | Carbamate | 301.33 | $C_{17}H_{19}NO_4$ | 1.00 |
| Flusilazol | Triazole | 315.40 | $C_{16}H_{15}F_2N_3Si$ | 0.20 |
| Flutriafol | Triazole | 301.30 | $C_{16}H_{13}F_2N_3O$ | 0.05 |
| Chlorothalonil | Chloronitrile | 265.90 | $C_8Cl_4N_2$ | 0.01 |
| Chlorpyrifos | Organophosphate | 350.59 | $C_9H_{11}Cl_3NO_3PS$ | 0.30 |
| Captan | N-trichloromethylthio | 300.59 | $C_9H_8Cl_3NO_2S$ | 5.00 |
| Krezoxim-methyl | Strobilurin | 313.30 | $C_{18}H_{19}NO_4$ | 0.05 |
| Penconazole | Triazole | 284.20 | $C_{13}H_{15}Cl_2N_3$ | 0.05 |
| Pymetrozine | Triazinone | 217.23 | $C_{10}H_{11}N_5O$ | 0.02 |
| Pyrimethanil | Anilinopyrimidine | 199.26 | $C_{12}H_{13}N_3$ | 0.05 |
| Tiophanate-methyl | Tiouree | 342.42 | $C_{12}H_{14}N_4O_4S_2$ | 0.30 |
| Trifloxystrobin | Strobilurin | 408.40 | $C_{20}H_{19}F_3N_2O_4$ | 1.00 |

*Official Journal of RS 25/2010 (Sl. Glasnik RS 25/2010)

The mass spectometer functions in the supervisng reaction mode SRM. For collection and processing of the data Agilent MassHunter B.03.02 was used. Carrier gas was helium, purity 99.9999% with a flow rate of 1 ml/min and the collision gas is nitrogen, purity 99.999% at a pressure of 2.8×10-3 mbar in the collision cell. Chromatographic separation is done on silica HP-5MS capillary column (30m×0.25mmx0.25mm). Temperature program was: initial temperature 70 °C maintained for 1 minute; the temperature rise of 50 °C/min to 150 °C; repeated rise of 6 °C/min to 200 °C; the final temperature rise of 16 °C/min to

280 °C, maintained for 2 min. 1 μl of sample is injected in splitless mode. Interface temperature was set to 250 °C and time set for cutting off the solvent was 6 minutes. EI type of ionization was used with temperature setting for ion source at 250 °C.

**Validation parameters**

**The detector linearity response was checked by preparing** the blank cherry sample to which an internal standard PCB 52 was added according to the QuEChERS method and after the evaporation the residue was diluted in 2 ml of the pesticide mixture standard in mass concentrations of 50, 100, 200, 500, 700 and 1000 μg/ml. The calibration of pesticides in the sample matrix was carried out in that manner.

**The recovery** was checked by enriching 10 g of a blank sample with the mixture of pesticide standard of 10 μg/ml in the amount of 50, 100 and 500 μl, with the addition of the internal standard PCB 52. The recovery was checked for the final mass concentration of 0.05, 0.10 and 0.50 μg/kg. The QuEChERS extraction was carried out from 10 g of the enriched sample with the addition of 10 ml acetonitrile. After being shaken in a vortex mixer (3 minutes) 6 g of $MgSO_4$, 1.5 g NaCl, 1,5 g trisodium citrate dehydrate and 0.75 g disodium hydrogen citrate sesquahydrate were added to the sample. After shaking and cetrifugation (5 min at 3000 rot/min), 5 ml supernatanta was mixed with a 1.5 g of $MgSO_4$, 0.25 g PSA and 0.01 g of active charcoal. On the repeated cetrifugation 2 ml supernatanta was evaporated to dryness and reconstituted in 2 ml of acetone.

**Reproducibilityof the method** was determined by analyzing the sample of the same mass concentration level (0,1 μg/kg) in six replicates and shown through the relative standard deviation - RSD (%).

**The limits of detection (LOD)** were calculated by means of „Calculate Signal-to-Noise“calculator within Qualitative MussHunter B.03.01 program (Agilent Technologies, 2010) based on the relation of standard deviation of the peak hight and noise hight in the chromatograms for the pesticide mixture dtsndsrd in the mass concentration of 0.01 μg/ml.

**The limits of quantification (LOQ)** were determined by adding 100 μl of pesticide mixture standard in the concentration of 1.0 μg/ml, in 10 g of the sample in six replicates.

## RESULTS AND DISCUSSION

The development of the method for the determination of the studied analytes in cherries comenses with GC-MS/MS optimization. The selection of the appropriate MRMs (multiple reaction monitroring) has to be approached carefully for each pesticide sa as to providr sufficient selectivity and specific features (Walorczyk, 2008). Firstyl the mass srectar of each pesticide is recorded in the ”scan” mode with the most intensive ions being chosen as product ions whereas by changing the energy of a collision sell in the ”precursor ion” modu,

the precusor ions are detected. Based on the obtained data the MRM transitions shown in Table 2 are formed while in Figure 1 there are overlapped MRM chromatograms of the studied pesticides. Two MRM tranzitions were used for the analysis of each analyte when one was used for the quantification and the second for the confirmation SANCO 657/2002.

Table 2. Target and qualifier transitions (MRM) for 17 pesticides

| Pesticides | Precursor-Product Ion | CE (eV) | Rt (min) | $R^2$ (0.05-0.10 μg/ml) |
|---|---|---|---|---|
| Azinphos-methyl | 160.1→132.1<br>160.1→105 | 20<br>20 | 25.70 | 0.997 |
| Boscalid | 344→342<br>344→142 | 15<br>15 | 9.60 | 0.994 |
| Bupirimate | 273→193<br>273→108 | 10<br>15 | 20.06 | 0.996 |
| Cypermethrin 1,2,3 | 181.1→152.1<br>181.1→127.1 | 30<br>35 | 18.8<br>20.04<br>23.78 | 0.994 |
| Difenoconazol | 265→139<br>323→265 | 25<br>15 | 19.20 | 0.997 |
| Dimethoate | 125→79<br>125→63 | 10<br>10 | 23.66 | 0.998 |
| Fenarimol | 139→111<br>139→75 | 15<br>35 | 18.76 | 0.999 |
| Flusilazol | 233→165<br>233→152 | 15<br>15 | 20.20 | 0.999 |
| Flutriafol | 219→123<br>219→95 | 15<br>25 | 19.83 | 0.999 |
| Chlorothalonil | 266→168<br>266→133 | 35<br>35 | 16.43 | 0.997 |
| Chlorpyrifos | 291.1→109<br>196.9→168.9 | 10<br>15 | 17.99 | 0.998 |
| Captan | 79.1→77.1<br>79.1→51.1 | 10<br>25 | 12.79 | 0.993 |
| Krezoxim-methyl | 206→116<br>206→131 | 5<br>10 | 20.00 | 0.999 |
| Penconazole | 248→192<br>248→157 | 10<br>20 | 18.79 | 0.999 |
| Pyrimethanil | 198→182<br>198→156 | 18<br>25 | 16.30 | 0.999 |
| Trifloxystrobin | 206→116<br>190→130 | 5<br>5 | 21.41 | 0.999 |
| PCB 52 | 291.4→222<br>291.4→220 | 28<br>28 | 16.76 | |

The method was validated by the analyses of linearity, recovery, reproducibility and quantification limit. All the quantitative results were calculated using the matrix enriched by standard prepared in such a way that the original sample was enriched by various concentration levels of pesticides such as opino in validation parameters. Thus, the matrix effect on the studied pesticides ,which can occur, is avoided.

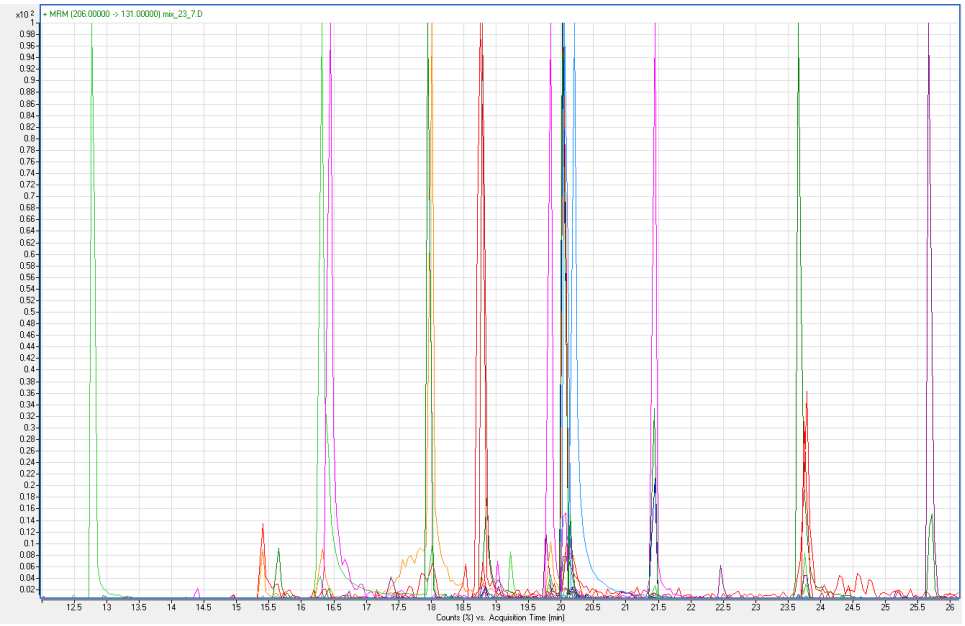


Figure 1: Overlapping MRM chromatograms

Table 3. Validation parameters

| Pesticides | Average recovery, % (RSD, %) | Repetability (RSD, %) | LOQ (µg/kg) |
|---|---|---|---|
| Azinphos-methyl | 102.4(10) | 8.92 | 0.01 |
| Boscalid | 91.5 (7) | 8.14 | 0.03 |
| Bupirimate | 95.8 (9) | 7.96 | 0.01 |
| Cypermethrin | 85.1 (12) | 11.14 | 0.01 |
| Difenoconazol | 87.2 (9) | 9.27 | 0.01 |
| Dimethoate | 77.5 (11) | 10.04 | 0.01 |
| Fenarimol | 101.3 (4) | 4.27 | 0.01 |
| Flusilazol | 100.9 (7) | 6.58 | 0.01 |
| Flutriafol | 99.7 (8) | 7.58 | 0.01 |
| Chlorothalonil | 99.2 (6) | 10.14 | 0.01 |
| Chlorpyrifos | 101.4 (6) | 7.17 | 0.01 |
| Captan | 81.2 (11) | 9.88 | 0.03 |
| Krezoxim-methyl | 84.5 (9) | 11.25 | 0.01 |
| Penconazole | 96.2 (4) | 6.37 | 0.01 |
| Pyrimethanil | 98.2 (7) | 9.17 | 0.01 |
| Trifloxystrobin | 97.9 (6) | 5.48 | 0.01 |

A good linearity was obtaioned for all the analyzed pesticides ranging from 0.05 to 1.00 µg/ml (which corresponds to 0.05 to 1.00 mg/kg in cherry matrix). The correlation coefficient of linearity ($R^2$) was above 0.99 for all the studied pesticides (Table 2.). The recovery was analyzed for three concentration levels in three replicates. The obtined results show that the reovery of the method ranged from 77.5 to 102.4% with RSD lower than 20%, which is in accordance

with the demands of the regulation SANCO/10684/2009. The reproducibility was analyzed at one concentration level in six replicates with RSD < 11.14%. The quantification limit was set and determined by experiments at the level of 10 μg/kg except for boskalid and kaptan (30 μg/kg).

The correlation coefficient of linearity (R2) was above 0.99 for all the pesticides (Table 2). Extraction yield was examined for three levels with three replications. The results show that the yield of method ranged from 77.5 to 102,4% with RSD less than 20%, which is in accordance with the requirements of regulation SANCO/10684/2009. Repeatability was tested at a concentration level in six repetitions with RSD < 11.14%. Limit of quantification was also established and experimentally determined at the level of 10 μg/kg, except for boscalid and captan (30 μg/kg).

## CONCLUSIONS

This paper delt with the possibility of the gas chromatography application with the tandem mass spectometry for the simultaneous residue determionation of 17 pesticides in cherries. Durin the optimization of the method the sample preparation implied the QuEChERSpreparation method with GC-MS/MS for the quantification and confirmation of pesticides. The calibration was carried out in cherry matrix in order to overcome the matrix effect. The correlation coefficients were higher than 0.99 for all the studied pesticides ranging from 0.05 to 1.0 μg/ml. The obtained mean values of the responds were in the range from 77. 5 to 102.4% with RSD lower than 20%. The reproducibility of the method expressed as a relative standard deviation was lower than 11.14%. The quantification limits were analyzed at the level of 0.01 mg/kg when all the pesticides were as demanded except for boscalide and captan. An efficient, sensitive and reliable method is developed which can be applied in the analysis of real samples to pesticide residues in cherries.

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***Vojislava BURSIĆ, Gorica VUKOVIĆ, Bojana ŠPIROVIĆ, Sanja LAZIĆ, Mira PUCAREVIĆ, Tijana ZEREMSKI***

## QuEChERS METOD ZA ODREĐIVANJE OSTATAKA PESTICIDA U TREŠNJAMA


### SAŽETAK

Razvijen je jednostavan multirezidualan metod za određivanje ostataka peticida u trešnjama, korišćenjem GC-MS/MS. Za analizu obojenih matriksa, poput trešanja, korišćen je modifikovan QuEChERS metod. Ovaj metod ekstrakcije podrazumeva ekstrakciju uzorka acetonitrilom, tokom tri minuta na vorteks mikseru, uz upotrebu soli, koristeći bezvodni magnezujum sulfat, natrijum hlorid, trinatrijum citrat dihidrat i dinatrijum hidrogen citrat seskvihidrat. Nakon mućkanja i centrifugiranja, prečišćavanje je izvedeno dodavanjem bezvodnog $MgSO_4$, PSA i aktivnog uglja u 5 ml ekstrakta. Nakon ponovljenog centrifugiranja, 2 ml ekstrakta je upareno do suva i rekonstituisano u 2 ml acetona. Optimizovani analitički uslovi su podrazumevali proveru prinosa ekstrakcije, ponovljivosti, granice detekcije i uticaj matriksa za 17 pesticida. Neki značajni uticaji matriksa su eliminisani upotrebom kalibracije pesticida u matriksu uzorka. Linearnost je ispitana u opsegu od 0,05 do 1,0 μg/ml sa $R^2$ višom od 0,99. Prinosi ekstrakcije su dobijeni obogaćivanjem blank uzorka na tri koncentraciona nivoa (0,05; 0,1 i 0,5 mg/kg) uz postizanje prinosa u intervalu od 77,5-102,04. Vrednosti ponovljivosti metode su bile niže od 11,14% za intradnevnu preciznost. Postavljene LOQ vrednosti su bile 10 μg/kg.


**Ključne riječi**: QuEChERS, ostaci pesticida, trešnje, GC-MS/MS.