

NOTE

Rapid Analysis of Indoxacarb Residues in Vegetable by QuEChERS and LC-MS/MS

HUA SHAO*, MAO-JUN JIN, FEN JIN, YU-TING HUANG, JING WANG and YING LI

Institute of Quality Standards & Testing Technology for Agro-products, Chinese Academy of Agricultural Sciences, Key Laboratory of Agrifood Safety and Quality, Ministry of Agriculture, Beijing 100081, P.R. China

*Corresponding author: E-mail: nkshaohua@163.com

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A method for determination of indoxacarb residues in vegetable was established by QuEChERS and LC-MS/MS. The average recovery of this method was in the range from 74.2-106.5 % at the spiked level of 0.2, 0.4 and 0.8 mg/kg into samples and the RSDs were in the range from 1.9-10.2 %. The linearity of method was good from 0.05-2 mg/L and limit of quantification (LOQ) was 0.05 mg/kg. This method is simple, rapid and applicable for rapid analysis of indoxacarb residues in vegetable.

Key Words: QuEChERS, Dispersive solid phase extraction, Rapid analysis, Vegetable, Indoxacarb.

Indoxacarb, produced in 1992 by DuPont, registered and listed in 2001, is a new oxadiazine insecticide. It has been widely used as an insecticide against many insects such as lepidoptera and other pests in vegetables¹⁻⁸. In China, indoxacarb has been used for controlling insect pests of rice, cotton and cruciferous vegetables. Therefore, it is essential to develop a sensitive and selective method for determination of indoxacarb residues in vegetables. The QuEChERS method makes it easier, quicker and less expensive to examine chemicals in food than other pretreatment methods and has been successfully used for the extraction and purification of a variety of chemicals in many matrices⁹⁻¹⁶. In this paper we developed a simple, rapid, sensitive and selective method based on QuEChERS and LC-MS/MS for the analysis of indoxacarb residues in vegetables.

HPLC-grade acetonitrile, methanol were obtained from Fisher Scientific (Pittsburgh, PA). Acetic acid (content > 99.7 %) of HPLC grade were purchased from DIMA Technology (Richmond Hill, Ontario, Canada). Sodium chloride and anhydrous magnesium sulfate of analytical grade were obtained from the Chemical Reagent Company (Beijing, China). Anhydrous magnesium sulfate had been heated at 500 °C for at least 4 h, cooled naturally and stored in desiccators. Primary secondary amine (PSA) sorbents were obtained from Agela Technologies (Beijing, China). Indoxacarb standard (purity = 95 %) was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Sample extraction and cleaning: A fully chopped and homogenized sample (10 g) was weighed into a 50 mL plastic

centrifuge tube. With the addition of 10 mL acetonitrile, the tube was vigorously shaken. Afterward, 4 g of anhydrous magnesium sulfate and 1g sodium chloride were added and the solution was shaken immediately for 1 min, then homogenized and centrifuged for 3 min at 5000 rpm. A total of 2 mL of the clarified supernatant was transferred into a clean plastic centrifuge tube containing 100 mg of primary secondary amine sorbents and 300 mg of anhydrous magnesium sulfate. The mixture was then shaken for 0.5 min, centrifuged for 1 min at 5000 rpm and finally, filtered through a 0.22 µm membrane for HPLC-MS/MS analysis.

Chromatographic condition: An Agilent series 1200 HPLC system (Agilent, Santa Clara, CA) .Which consisted of a binary pump, a column oven and an auto sampler. Separation was carried out on a Waters SunFire C₁₈ analytical column (150 mm × 4.6 mm × 5 µm) (Milford, MA, USA). The mobile phases consisting of mobile phase A (0.1 % acetic acid in pure water) and mobile phase B (0.1 % acetic acid in methanol) were used with 10:90. The injection volume was 10 µL and the column temperature was maintained at 30 °C.

Mass spectrometric conditions: An API 2000 tandem quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) with an electrospray (ESI) ionization source. Typical ESI parameters were used as follows: the MRM transitions; ion spray voltage (IS), 5500 V; atomization air pressure (GS1), 40 psi; auxiliary gas (GS2), 50 psi; curtain gas (CUR), 10 psi; ion source temperature (TEM), 500 °C; entrance potential (EP), 12 V; collision cell exit potential (CXP), 4 V and declustering potential (DP), 35 V. The entrance and collision cell exit

potentials were set at 12 and 4 V. The collision energy was set at 33, 26 and 20 V for different daughter ions 218.2, 249.1 and 293.1, respectively.

Optimization of LC-MS/MS conditions: Using a Q1 scan in infusion experiments, $[M + H]^+$ was selected as the precursor ion for indoxacarb (m/z 528.0). The precursor ion product transition m/z 528.0 \rightarrow 218.2 which was with highest intensity, was selected for quantitation. In addition to m/z 528.0 \rightarrow 218.2, the transition m/z 528.0 \rightarrow 249.1 and 528.0 \rightarrow 293 were the higher intensity than others, thus, were chosen as firmative transition.

Method validation: Under the optimal conditions, the linear calibration curves were constructed from calibration solutions in extracts of two representative, blank matrices (spinach, broccoli), at six different concentrations (0.05, 0.1, 0.2, 0.5, 1 and 2 mg/ L) in the range of 0.05-2 mg/ L for indoxacarb. Both correlation coefficients (r^2) were 0.9998. The accuracy of the method was verified by measuring recoveries from spiked blank samples of the different matrices investigated at three concentration levels, 0.2, 0.4 and 0.8 mg/kg, three replicates at each fortification level. As shown in Table-1, satisfactory method recoveries were obtained for indoxacarb spiked at three concentration levels in spinach samples [74.2-85.7 %, relative standard deviation (RSD) < 5.1 %] and broccoli samples (93.3-106.5 %, RSD < 10.2 %). The limit of quantification (LOQ) and limit of detection (LOD) of indoxacarb were estimated by analyzing spiked samples at low concentrations. Representative MRM chromatograms of blank broccoli spiked with 0.05 mg/kg indoxacarb are shown in Fig. 1. LOQ (S/N = 10) was 0.05 mg/ kg and LOD (S/N = 3) was 0.02 mg/kg. LOQ was lower than the maximum limit of residues established for indoxacarb.

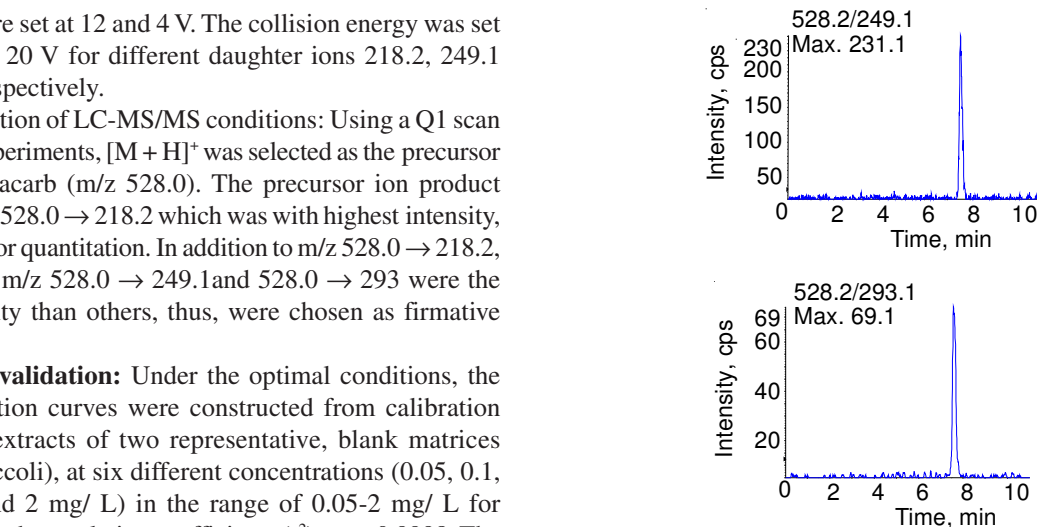


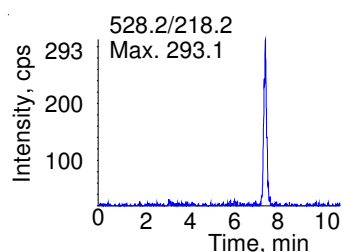
Fig. 1. Representative MRM chromatograms of blank broccoli spiked with 0.05 mg/kg Indoxacarb

Conclusion

A simple and rapid method for the quantitative determination of indoxacarb residues in vegetables was developed by QuEChERS and LC-MS/MS. This method was validated with fortified samples with excellent recovery and RSD were obtained. LOQ was lower than the maximum limit of residues established for indoxacarb.

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Matrix name	Spiked level (mg/kg)	Recovery (%)	RSD (%)	LOQ (mg/kg)	LOD (mg/kg)
Spinach	0.2	85.7	1.9	0.05	0.02
	0.4	74.2	2.5		
	0.8	76.5	5.1		
Broccoli	0.2	93.3	8.9	0.05	0.02
	0.4	106.5	10.2		
	0.8	96.4	4.2		