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Analytical Methods

Determination of metrafenone in vegetables by matrix solid-phase dispersion and HPLC-UV method

Jianjun Li [a,b,*], Yangyang Li [c], Dongliang Xu [b], Jingyu Zhang [b], Yuxi Wang [b], Chao Luo [b]

[a] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Northwest University, Xi'an 710069, China
[b] National Engineering Research Center for Miniaturized Detection Systems, Xi'an 710069, China
[c] Xi'an Municipal Public Security Bureau Legal Medical & Chemistry Technical Section, Xi'an 710069, China

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ABSTRACT

A simple method for determination of metrafenone in vegetables by matrix solid-phase dispersion (MSPD) and HPLC was developed. All vegetable samples were extracted with dichloromethane, and then the extracts were directly separated on a reversed-phase column with isocratic elution without a cleanup step. The linearity of metrafenone was good with the concentration between 0.005 and 5 mg/kg, and the limit of detection (LOD) of the metrafenone was 0.002 mg/kg. The recoveries ranged from 86.5% to 104.8% with the relative standard deviations (RSDs) in the range of 2.1–7.9% (n = 6). The results indicated that the method was simple, rapid, highly sensitive and suitable for the determination of metrafenone in vegetables.

1. Introduction

Metrafenone (3′-bromo-2,3,4,6′-tetramethoxy-2′,6-dimethyl benzophenone; Fig. 1) was a new kind of benzophenone fungicide developed by BASF company in Germany. It had been registered in countries including UK and the Netherlands since 2003. Different from many existing commercial fungicides' mechanism of action, metrafenone had preventive, curative, uprooting and antisporulant effects against various types of powdery mildew. Metrafenone could keep mycelium from growing normally, controlling and preventing the invasion of powdery mildew effectively (Krystina et al., 2006). Therefore, it had been used to prevent and cure powdery mildew and eye spot in crops including grains, grapes and cucumbers. In the European Union, the European Food Safety Authority (EFSA) had recently modified the existing maximum residue level (MRL) of metrafenone in various crops, which range from 0.01 to 2 mg/kg depending on the crop. (1.7.2015 EN Official Journal of the European Union L 167/10; European Food Safety Authority, 2013).

Up to date, the majority of studies were focused on the efficacy of metrafenone (Capriotti, Gentili, Vecchio, Balzaretti, & Fagnani, 2006; Felsenstein, Semar, & Stammler, 2010; Gong et al., 2013; Krystina et al., 2006; Regueiro, Olguín, Simal-Gándara, & Sunol, 2015), but few articles on the detection measures on metrafenone had been reported. The QuEChERS method (Anastassiades & Lehotay, 2003) which was an AOAC official method for multi-residue detection could be used for residue analysis of metrafenone. The method based on liquid chromatography coupled with tandem mass spectrometry detection (LC-MS/MS) was validated in high water (cucumbers), high acidic (lemons), high oil (oilseed rape) content and dry commodities (dry beans, hops, wheat grain and straw) with a limits of quantification (LOQ) of 0.01 mg/kg. In this method, the extraction process was relatively complex and a cleanup step was also necessary. In addition, a slight adjustment of the method was necessary for different crops, which required high professional skills for experimenter. Zhu, Zhao, Feng, and Kim (2014) did researches on 227 pesticides in pepper samples with high performance liquid chromatography–mass spectrometry (HPLC–MS). The pepper samples were first extracted with DisQuE QuECHERS using a method including acetonitrile and dispersive SPE with 10 g of MWCNTs used for the cleanup procedure. After filtering, the eluted residues were used in LC–MS/MS analyses. The range of recovery rate is 70–120%, while there were no details about the research on metrafenone and the pretreatment process was very tedious. Wang, Liu, and Sun (2016) put forward a detection on metrafenone in bitter gourds and soil samples with gas chromatography (GC), in which ethyl acetate was used to extract metrafenone from samples, then metrafenone was cleaned up by Florida silica and amino solid-phase extraction (SPE) and was

* Corresponding author at: Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Northwest University, Xi'an 710069, China.
E-mail address: bootan12@126.com (J. Li).

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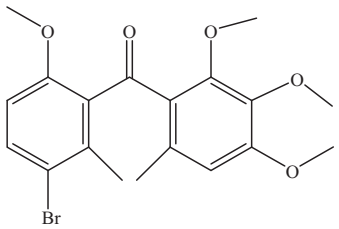

Fig. 1. Chemical structures of metrafenone.

finally detected with an ECD detector. The measurement needed a great deal of organic solvent in the treating procedure that was tedious and time-consuming. Kabir et al. (2016) also developed a GC-ECD method to detect metrafenone residues and estimate the half-lives in lettuce. Samples were extracted with acetone and matrix components were purified using a silica solid-phase extraction (SPE) cartridge. The LOD and LOQ were 0.003 and 0.01 mg/L, respectively. Recoveries ranged from 78.5 to 113.3% with a relative standard deviation <8%. In this method, the ample extraction process was considerably complex, time-consuming and a cleanup step was needed.

Matrix solid-phase dispersion (MSPD), a new extraction technology based on SPE (Barker, 2000; Barker, Long, & Short, 1989), was applied to the pre-process of solid, semi-solid and high-viscosity biological samples. At present, MSPD was a hotspot in the research on the sample pretreatment in analyzing tests (Duarte et al., 2013; Gañán et al., 2014; Salemi, Shafiei, & Vosough, 2012; Shen, Jin, Xue, Lu, & Dai, 2016; Ziarrusta et al., 2015). It was simpler in operation than SPE. The procedures of MSPD were as follows: Sample was grinded with the dispersants directly in a mortar with a pestle. After blending, the homogenized mixture was transferred in a solid-phase extraction cartridge, and compressed. A suitable solvent or solvent mixture was then used to elute the determinant. Depending on the mechanical shear force of filler particles, MSPD shortened the processes of blending, tissue cell lysis, extraction and purification in the pretreatment of conventional sample, in which the loss of determinant was avoided in blending, dissolution, emulsification and concentration.

The aim of this study was to develop a simple and fast method for in the detection of metrafenone in vegetables by MSPD-HPLC. In this study, the metrafenone was extracted from vegetable samples with dichloromethane in MSPD and detected successfully by HPLC. This method has advantages of quick, easy, high sensitivity, good repeatability and accuracy. It was suitable for large quantities of analysis and met the technical requirements for residue detection in vegetables.

2. Materials and methods

2.1. Instrument, standards and reagents

Measurements were carried out by the injection of 10 μL of the sample into an Agilent 1260 Series LC system (Agilent Technologies, America) consisting of a membrane degasser, a binary high-pressure gradient pump, a high performance auto sampler, a UV-detector and a column thermostat. The chromatographic separation was achieved on a Zorbax Eclipse Plus C18 column (4.6 mm × 250 mm, 5 μm, Agilent) equipped with a Security Guard (2.0 mm × 4 mm, AQ C18, America). A MTN-2800D termovap sample concentrator from Beijing Huaruiboyuan Technology Manufacturing Co., Ltd. (China) was used. The Miccra D-8 homogenizer was obtained from ART Co., Ltd. (Germany). BT 125D electronic balance (Sartorius, Germany) was used. MS3 basic vortex mixer (IKA, Germany) was used. Ultra-pure water was prepared by Milli-Qpurifier (Millipore, America).

The analytical standard metrafenone (99.7% purity) was purchased from Dr. Ehrenstorfer GmbH (Germany). Acetonitrile (chromatographically pure, Sigma, USA), Neutral alumina, silica gel, dichloromethane, ethyl acetate, activated carbon(all analytical grade reagents) were purchased from Sinopharm Chemical Reagents Co., Ltd (Shanghai, China).

2.2. Preparation of samples and spiked samples

All fresh vegetable samples were purchased from local supermarkets. These vegetable samples were cut into smaller pieces according to the method of coning and quartering (WuHan University, 2000). Samples of 0.5 kg were homogenized in a homogenizer, and stored at -20 °C until analysis.

Spiked samples were acquired via appropriate dilution of the stock solutions into 0.2 kg the above blank samples pulp, homogenized and stored at -20 °C until analysis.

2.3. MSPD process

First, 2.0 g homogenized vegetable sample, 8 g solid-phase extracted dispersant were placed into a mortar and blended using a pestle until a visually homogeneous mixture was obtained. Following complete dispersal, the homogeneous mixture was transferred into a 20 mL syringe with two frit disks packed at the bottom and at the top of the sample mixture. Then the target analytes were then eluted four times with 30 mL dichloromethane and the eluent was collected in a 50 mL centrifuge tube. To achieve dryness, the eluent was blow-dried with N_2 at room temperature and the residue was reconstituted with 0.5 mL of acetonitrile and filtered through nylon filters (0.22 μm) prior to the HPLC-UV analysis.

2.4. Chromatographic conditions

Analysis was performed using an Agilent 1260 Series LC system equipped with UV-detector and a Zorbax Eclipse Plus C18 column (4.6 mm × 250 mm). The chromatogram was recorded at 285 nm and the peak areas were quantified. The mobile phase was ACN/H2O (70:30, v/v) and maintained at 1.0 mL min^{-1}. Sample injection volume was 10 μL and column thermostat temperature was 25 °C.

2.5. Preparation of standard solutions

Stock solution of metrafenone (1000 μg/mL) was prepared by dissolving 25.08 mg of metrafenone in 25 mL acetonitrile. Working solution was prepared by further dilution the stock solution in acetonitrile to 0.05, 0.4, 1.0, 5.0, 10.0 and 50.0 μg/mL.

3. Results and discussion

3.1. Selection of detection wavelength

The molecular structure of metrafenone contains benzene ring, which had absorption in the ultraviolet region. The maximum absorption wavelength was 225 nm. When the wavelength was 285 nm, there was relative larger absorption. To reduce the interference of the solvent, the 285 nm wavelength was chosen in the experiment.

3.2. Selection of the elution solvent

The selectivity of an MSPD procedure depended on the sorbent/solvent combination used. The nature of the elution solvent was important since the target analytes should be efficiently