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Ultra performance liquid chromatography-tandem mass spectrometry for the determination of amicarthiazol residues in soil and water samples

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ABSTRACT

A reliable and rapid method has been optimized to determine the residue of amicarthiazol in soil and environmental water samples. After extraction and evaporation, the extraction was carried out with solid phase extraction (SPE) cleanup using HLB cartridge (only soil samples) and for the quantitative determination by ultra performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). The resulting residues of amicarthiazol were analyzed by a gradient separation performed on a UPLC system with a C_{18} column, methanol and water containing 0.1% ($v\ v^{-1}$) formic acid as the mobile phase in the mode of electrospray positive ionization (ESI^+) and multiple reaction monitoring (MRM). Results showed that the recoveries for spiked samples were 74.4–97.1% and 72.1–109.9% for soil and water, respectively, with the relative standard deviation (RSD) less than 10.2% when fortified at 10, 100 and 1000 $\mu g\,L^{-1}$. The limits of detection (LODs) and the limits of quantification (LOQs) for matrix matched standards ranged from 0.073–0.425 $\mu g\,L^{-1}$ and 0.243–1.42 $\mu g\,L^{-1}$. The intra-day precision ($n = 5$) and the inter-day precision over 10 days ($n = 10$) for the amicarthiazol in soils and water samples spiked at 100 $\mu g\,L^{-1}$ was 7.9% and 15.9%, respectively. Results indicated that the developed method could be a helpful tool for the controlling and monitoring of the risks posed by amicarthiazol to human health and environment safety.

1. Introduction

Amicarthiazol (2-amino-4-methyl-carboxanilithiazol) (Fig. 1), a kind of amide fungicides (bactericide), contains both groups of carboxylamide and thiazole, possessing not only the biological activities of carboxylamide fungicides for controlling basidiomycetous diseases but also those of thiazole bactericides against bacterial diseases [1]. As a systemic fungicide, amicarthiazol is widely applied on rice, wheat, cotton, citrus and tobacco in China [2]. This fungicide was generally applied as seed treating agent, despite that several formulations of it were registrated as plant spraying agents recently [3]. Frequent application of this fungicide poses a potential risk to either environmental bio-species [4] or human beings. However, to the best of our knowledge, the maximum residue limits (MRLs) of amicarthiazol is still not well-established globally.

Traditionally, the analytical methods for the analysis of residual amicarthiazol in capsicum, soil [5,6] and tobacco seedlings [2] samples were developed using high performance liquid chromatography (HPLC), requiring several steps and large quantities of solvents for sample preparation and extraction of the analytes. Recently, Ultra Performance Liquid Chromatography-tandem Mass Spectrometry (UPLC-MSMS) was frequently adopted to analyze trace amounts of pesticides in environmental matrices. Neverthless, studies with respect to analysis of amicarthiazol by this high-performance technique is poorly reported.

Solid-phase-extraction (SPE) method, as is known, can be used to extract and pre-concentrate a wide array of compounds [7] and reduce matrix effects (signal suppression or enhancement) in a single fashion for the UPLC-MS/MS analysis [8]. Another advantage of SPE is that it can be automated, either off-line [7] or on-line [9,10], greatly reducing the involvement of manual operation and thus increasing the reproducibility of extractions through tight control of variables, such as flow rates, solvent volumes, and equilibration and drying times [11].

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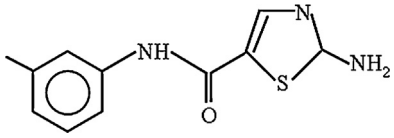

Fig. 1. Chemical structure of amicarthiazol.

Nowadays, LC-MS/MS is becoming one of the powerful techniques for the residue analysis of polar, ionic or low volatility fungicides in fruits and vegetables [12]. Especially HPLC-MS/MS has proven to be a powerful tool for trace analysis due to its high selectivity, precision and sensitivity [13]. Among the several ionization modes, electrospray ionization (ESI) has proven to be a reliable, robust and sensitive mode [14–16]. In MS/MS the use of multiple reactions monitoring (MRM) mode permits a significant decrease in the detection limits, owing to the increased signal-to-noise ratio. In contrast to conventional HPLC, a recently developed technology termed UPLC has been applied to pesticide residue detection, and provided a higher peak capacity and a faster speed of analysis [17,18]. Here, a rapid, sensitive and reliable method for analysis of amicarthiazol residues in soil and water was developed. As far as we know, this was the first report of quantitative analysis of amicarthiazol residues in the environment using UPLC-MS/MS.

2. Experimental

2.1. Reagents and materials

Analytical standard of amicarthiazol (99.5% purity) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). Formic acid was obtained from Tedia (Fairfield, USA). Water was processed with a Milli-Q water purification system (Millipore Corp, USA) and used to prepare all aqueous solutions.

Five soil and five water samples from different locations were used in the present study. All samples were free of amicarthiazol residue by HPLC. Five soil samples were collected from Wuxi (Jiangsu province, paddy soil), Quzhou (Zhejiang province, red soil), Harbin (Heilongjiang province, black soil), Jiaxing (Zhejiang province, moisture soil) and Hangzhou (Zhejiang province, powder soil). Samples were air dried and then passed through a 2 mm sieve for removal of particles and non-decomposed plant residues. The prepared soil samples were stored at room temperature during the studies. The properties of the five soil series are presented in Table 1.

Five water samples were taken in different regions: lake water (from West Lake, Hangzhou, pH 6.5), river water (from Tiesha river, Hangzhou, pH 6.0), pond water (from Qizhen lake, Hangzhou, pH 6.0), spring water (from Hupao Spring, Hangzhou, pH 5.5), and tap water (pH 6.8). All water samples were collected in amber polyethylene terephthalate (PET) bottles and transported to the laboratory at 4 °C in the dark.

Table 2
Gradient elution of UPLC.

Time (min)	Flow rate (mL/min)	Eluent A[a] (%)	Eluent B[b] (%)	Curve[c]
Initial	0.2	40	60	Initial
2.5	0.2	20	80	1
3.0	0.2	20	80	6
3.5	0.2	40	60	6

[a] Eluent A: 0.1% (v/v) formic acid in ultrapurefied water.
[b] Eluent B: methanol.
[c] Mixing curve of mobile phases for Waters HPLC system, 1 means "immedieately goes to specified conditions" and 6 is a default value which means "linear effect".

2.2. Instruments

Centrifugation was performed in an Anke DL-5-B centrifuge (Shanghai flying pigeon company, China), Mechanical shaking extraction was used a constant temperature incubator shaker (Shanghai zhicheng analysis instrument manufacturing Co., Ltd., China). The rotary evaporator RE-2000 was purchased from Yarong biochemical instrument plant (Shanghai, China).

2.3. Preparation of standard solutions

Standard stock solution (1000 mg L^{-1}) was prepared by accurately dissolving 10.0 mg of the analyte in 10.0 mL of methanol and stored at 4 °C for no more than three months. The working solutions of amicarthiazol were prepared weekly by series dilution of stock solution in methanol at the concentrations ranging from 5 μg L^{-1} to 100 mg L^{-1} for sample fortification or optimization of experimental conditions. In order to optimize the extraction conditions and in the validation study in different concentration levels from 5 μg L^{-1} to 1000 μg L^{-1}, the calibration standards at the concentrations 5, 10, 50, 100, 200, 500 and 1000 μg L^{-1} were constructed by re-dissolution of matrix extracts of control samples in working standards directly.

2.4. UPLC-MS/MS analysis

Chromatographic analyses were conducted by using an Acquity Ultra Performance LC (Waters, USA). The analyte were separated on an ACQUITY UPLC® HSS T3 column (2.1 mm × 100 mm, with a 1.8 μm particle size. Waters, USA). The mobile phases consisting of eluent A (0.1% formic acid in ultrapure water) and eluent B (methanol) were used with a gradient elution (shown in Table 2). The injection volume was 10 μL, and the column temperature was maintained at 30 °C.

Mass spectrometric detection was carried out by using a Triple quadrupole 5500 mass spectrometer (Applied Biosystems Sciex, USA) in positive multiple reaction modes (MRM). The instrument was equipped with an electrospray (ESI) ionization source. Typical ESI parameters were used as follows: ion spray voltage (IS), 3500 V; Atomization air pressure (GS1), 40.00 psi; Auxiliary gas (GS2), 50.00 psi; Curtain gas (CUR), 20.00 psi; Ion source temperature (TEM), 450 °C; Collision activated dissociation (CAD), 5.00 V; Entrance potential (EP). 3.00 V; Declustering potential (DP), 10.00 V and product ions at m/z 115 and 141, optimum collision energies were 28 eV, 30 eV, respectively. Instrument control and data

Table 1
Characterization for the five soils.

Resource	Texture class	pH	Sand (%)	Silt (%)	Clay (%)	Organic carbon (%)	CEC[a] (cmol kg^{-1})
Harbin	Black soil	7.80	39.7	43.9	16.4	2.94	22.2
Wuxi	Paddy soil	6.18	10.1	80.7	9.2	2.95	14.8
Jiaxing	Moisture soil	7.52	7.6	69.3	23.1	5.02	21.3
Hangzhou	Powder soil	6.80	21.5	71.1	7.4	3.10	10.6
Quzhou	Red soil	4.20	44.8	44.0	11.2	0.93	21.4

[a] CEC: cation exchange capacity.